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ABSTRACT

Hybrid materials of earth abundant transition metal dichalcogenides and noble metal nanoparticles, such as molybdenum sulfide (MoS_x) and gold nanoparticles, exhibit synergistic effects that can enhance electrocatalytic reactions. However, most current hybrid MoS_x -gold synthesis requires an energy intensive heat source of $>500^\circ\text{C}$ or chemical plating to achieve deposition of MoS_x on the gold surface. Herein, we demonstrate the direct overgrowth of MoS_x over colloidal nanoporous gold (NPG), conducted feasibly under ambient conditions, to form hybrid particles with enhanced electrocatalytic performance toward hydrogen evolution reaction. Our strategy exploits the localized surface plasmon resonance-mediated photothermal heating of NPG to achieve $>230^\circ\text{C}$ surface temperature, which induces the decomposition of the $(\text{NH}_4)_2\text{MoS}_4$ precursor and direct overgrowth of MoS_x over NPG. By tuning the concentration ratio between the precursor and NPG, the amount of MoS_x particles deposited can be systematically controlled from 0.5% to 2% of the $\text{Mo}/(\text{Au} + \text{Mo})$ ratio. Importantly, we find that the hybrid particles exhibit higher bridging and an apical S to terminal S atomic ratio than pure molybdenum sulfide, which gives rise to their enhanced electrocatalytic performance for hydrogen evolution reaction. We demonstrate that hybrid MoS_x -NPG exhibits $>30\text{ mV}$ lower onset potential and a 1.7-fold lower Tafel slope as compared to pure MoS_x . Our methodology provides an energy- and cost-efficient synthesis pathway, which can be extended to the synthesis of various functional hybrid structures with unique properties for catalysis and sensing applications.

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I. INTRODUCTION

Hybrid materials of earth abundant transition metal dichalcogenides and noble metal nanoparticles, such as molybdenum disulfide (MoS_2) and Au nanoparticles, feature enhanced performance in optical sensing and photo/electrocatalysis.^{1,2} This is due to the synergistic effect between dichalcogenides' optoelectronic properties arising from their tunable band gaps and high charge-carrier

mobility,³ and the high surface area-to-volume ratio as well as the localized surface plasmon resonance (LSPR) of Au nanoparticles.⁴ For example, hybrid MoS_2 films on nanoporous gold (NPG) have been demonstrated to exhibit high electrocatalytic activities toward hydrogen evolution reaction (HER).^{5,6} However, the fabrication of these platforms requires high temperature chemical vapor deposition up to 650°C for MoS_2 coating and are restricted to only pre-assembled 2D substrates as base templates.⁵ Although the chemical

plating method is able to deposit amorphous molybdenum sulfides MoS_x on nanoporous gold, it requires an additional chemical agent and is also performed on 2D gold membrane substrates.⁷ This makes such substrate-based hybrid platform preparation methods time-consuming and difficult to mass produce. On the other hand, the solution-phase preparation of colloidal hybrid MoS_x -Au forms freely dispersed particles that can be incorporated into any support

or substrateless platform (e.g. microfluidic devices) for various applications in reaction and analysis.⁸ However, this solution method also requires high temperature heating ($>500^\circ\text{C}$) to allow sulfide deposition onto the metal surface.⁸ Overall, the major bottleneck of current substrate-based and solution-phase methodologies is the high energy or chemical requirement to achieve the deposition of the secondary material. Thus, this raises the need for greener

FIG. 1. Overview, nanoporous gold bowl (NPG), and its surface temperature during irradiation. (a) Overview scheme of colloidal synthesis of hybrid MoS_x -nanoporous gold bowl (MoS_x -NPG) particles with enhanced hydrogen evolution reaction (HER) catalytic activity. The synthesis is performed by thermal decomposition of $(\text{NH}_4)_2\text{MoS}_4$ under ambient conditions by the photothermal effect of NPG. (b) SEM images of the as-prepared NPGs under (i) low magnification and (ii) high magnification of the yellow-dotted region in (i). (c) Distribution bar graphs of (i) diameter and (ii) ligament size of NPGs. (d) Extinction spectrum of colloidal NPGs. (e) (i) Scheme illustrating the photothermal effect of NPG in achieving a surface temperature of $\geq 230^\circ\text{C}$ that can polymerize soybean oil glycerides, upon light irradiation. (ii) Raman spectra of soybean oil during irradiation when mixed with NPGs, showing the increase in the aliphatic C-H peak over vinyl C-H peak, which indicates consistent polymerization of soybean oil glycerides.

methods that can be performed under ambient conditions, to be applied in both laboratory and industry-scale synthesis of these unique catalysts.

Herein, we demonstrate the direct overgrowth of molybdenum sulfide over colloidal NPGs, conducted feasibly in solution and under ambient conditions, to form hybrid particles with enhanced electrocatalytic performance toward HER. Our unique strategy exploits the localized surface plasmon resonance-mediated photothermal heating of the primary NPG material, NPG bowls (NPG), to induce the overgrowth of a secondary MoS_x layer and produce hybrid MoS_x -NPG particles without any additional chemical agent [Fig. 1(a)]. Such photothermal effect, achieved even at room temperature, can induce highly localized heating on the NPG surface to $\geq 230^\circ\text{C}$ and decompose the $(\text{NH}_4)_2\text{MoS}_4$ precursor to MoS_x without the need of bulk heating or autoclaves. Our method is an energy-saving and low-cost method that surpasses traditional methods, which require harsh synthesis/fabrication conditions. By tuning the concentration ratio between the $(\text{NH}_4)_2\text{MoS}_4$ precursor and NPG, the amount of MoS_x particles deposited can be systematically controlled from 0.5% to 2% of the $\text{Mo}/(\text{Au} + \text{Mo})$ ratio. We then characterize the morphology and chemical composition of the hybrid nanoparticles with transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma optical emission spectrometry (ICP-OES). More importantly, we showcase the enhanced electrocatalytic performance of our as-prepared MoS_x -NPG hybrid for hydrogen evolution reaction, which is a crucial process to generate hydrogen gas that is highly sought after as alternative energy sources. The hybrid MoS_x -NPG nanoparticles exhibit improved HER activity, achieving >30 mV lower overpotential and a 1.7-fold lower Tafel slope as compared to the control using pure MoS_x . Hence, our methodology provides an energy- and cost-efficient synthesis pathway, which can be extended to the synthesis of various functional hybrid structures with unique properties for catalytic and sensing applications.

II. RESULTS AND DISCUSSION

We begin by synthesizing bowl-shaped NPGs using a sacrificial template method.⁹ NPGs are grown at the corners of AgCl nanocube templates followed by etching of the AgCl nanocubes using aqueous ammonia solution. This results in bowl-shaped NPGs with a diameter of 678 ± 82 nm and a ligament size of 18 ± 4 nm, respectively [Figs. 1(b) and 1(c)]. Our NPG consists of bicontinuous porous Au nanostructures with manifold interconnected nanosized ligaments. This unique structure gives rise to strong and broadband of LSPR over a wide range from 400 to 1000 nm [Fig. 1(d)].^{9–11} The LSPR-enhanced electromagnetic field in NPG enhances its absorption of light, which results in nonradiative damping and generates abundant heat to elevate the NPG surface temperature.^{12–14} Moreover, the photothermal heating achieved by NPG is expected to surpass that of traditional smooth surface metal nanoparticles,^{12,14} owing to the much more intense SPR generated from the nanoscale ligaments. This makes NPG ideal for SPR-mediated photothermal chemical reactions and hybrid structure growth.⁵ As a demonstration, we probe the macroscopic temperature of a NPG substrate ($\sim 7.55 \mu\text{g mm}^{-2}$) under solar simulator irradiation using a thermal infrared (IR) camera (Fig. S1). Notably, we observe a rapid

rise in macroscopic temperature at a heating rate of $1.35^\circ\text{C s}^{-1}$, achieving the maximum macroscopic temperature of 46°C within 1 min. This clearly illustrates the intense and highly responsive photothermal effect of NPGs under solar irradiation, which can be further exploited as a thermal source to conduct reactions under ambient conditions.¹⁵ We also note that although the IR camera is able to measure the macroscopic temperature of the entire NPG-coated substrate, it does not represent the actual localized surface temperature on each NPG because of its limited camera resolution.¹⁶

To estimate the minimum localized surface temperature that NPG can achieve upon solar simulator irradiation, we perform an indirect temperature determination via *in situ* probing of the polymerization reaction of soybean oil [Fig. 1(d–i)]. Soybean oil, which is a mixture of triglycerides with unsaturated alkenes ($\text{C}=\text{C}$), undergoes thermal polymerization when heated above 230°C [Fig. 1(e–i)].¹⁷ This polymerization process can be monitored using Raman peaks of aliphatic $\text{C}-\text{H}$ bonds (2856 cm^{-1}) and vinyl $\text{C}-\text{H}$ bonds (3016 cm^{-1}),¹⁸ whereby the number of aliphatic bonds increases in the place of vinyl $\text{C}-\text{H}$ bonds as the alkenes polymerize. We disperse the NPGs in soybean oil and monitor the changes in the Raman peak intensity ratio of aliphatic $\text{C}-\text{H}$ and vinyl $\text{C}-\text{H}$ bonds during irradiation. We observe that the ratio of the aliphatic $\text{C}-\text{H}$ /vinyl $\text{C}-\text{H}$ peak intensities increases from 4.92 to 5.82 after 2 h of irradiation, indicating the ability of the NPG photothermal effect to successfully polymerize soybean oil [Fig. 1(e–ii) and Fig. S2]. Importantly, this observation demonstrates that the localized surface temperature of NPG is capable of reaching at least 230°C under solar simulator irradiation, which is also the temperature at which thermal decomposition of the molybdenum sulfide precursor to MoS_x occurs.¹⁹ We emphasize that this is not an absolute method to determine the exact local temperature that the NPG surface can achieve, but rather an estimate of the *minimum* temperature it can induce to the surrounding matter. Nevertheless, such efficient localized heating on individual particles in solution can be achieved on-demand by light irradiation at room temperature, which is highly advantageous for the solution-based hybrid material growth synthesis.

Next, we exploit the photothermal energy of NPG to decompose the $(\text{NH}_4)_2\text{MoS}_4$ precursor and deposit MoS_x directly onto the NPG surface [Fig. 2(a)]. The amorphous MoS_x formation is expected to occur in the temperature range 200°C – 250°C , as determined by thermogravimetric analysis [Fig. 2(b) and Fig. S3].²⁰ Hence, by mixing NPGs and $(\text{NH}_4)_2\text{MoS}_4$, we make use of the localized surface temperatures of $\geq 230^\circ\text{C}$ achieved by NPGs to directly deposit MoS_x particles onto their surface upon light irradiation. Briefly, we irradiate an aqueous mixture of NPGs and $(\text{NH}_4)_2\text{MoS}_4$ under solar simulation for 2 h. After the irradiation, a deposited layer of amorphous MoS_x can be observed on the surface of NPGs [as indicated by the arrows in Fig. 2(c)]. In order to investigate the effects of the precursor concentration on the overall hybrid nanostructure, we tune the $\text{Mo}/(\text{Au} + \text{Mo})$ ratio of the starting precursors at 0.5%, 1.0%, 1.5%, and 2.0%, which are denoted as 0.5% MoS_x -NPG, 1.0% MoS_x -NPG, 1.5% MoS_x -NPG, and 2.0% MoS_x -NPG, respectively. Overall, we notice a layer of MoS_x is deposited on the surface of NPGs across all ratios of MoS_x -NPG hybrids [Fig. 2(c) and Fig. S4]. As the ratio between MoS_x and NPGs increases from 0.5% to 2.0%, the thickness of the amorphous MoS_x increases gradually from 3 nm,

FIG. 2. LSPR-induced photothermal deposition of amorphous MoS_x onto the NPG surface to form hybrid MoS_x-NPG particles. (a) Scheme illustrating the photothermal deposition process. (b) Thermogravimetric analysis curve of (NH₄)₂MoS₄, indicating its decomposition at ≥ 200 °C. (c) Transmission electron microscopy (TEM) images showing amorphous MoS_x on the NPG surfaces of (i) 0.5%MoS_x-NPG and (ii) 2% MoS_x-NPG. (d) XPS characterization of MoS_x-NPG showing the presence of (i) Au 4f, (ii) Mo 3d, and (iii) S 2p in 0.5% MoS_x-NPG. (e) Graph comparing the ratios between the XPS S 2p peak area sum of bridging- and apical S ligands against the peak area sum of terminal S in various samples. (f) Graph comparing the XPS intensity ratios between S and Mo in various MoS_x-NPG samples and amorphous MoS_x sample.

5 nm, 7 nm to 10 nm This indicates that we can systematically vary the thickness of amorphous MoS_x by simply tuning the precursor concentrations.

To affirm the successful synthesis of MoS_x-NPG hybrid nanoparticles, we perform X-ray photoelectron spectroscopy (XPS) analysis of the nanoparticles to reveal the presence of all 3 elements of Au, Mo, and S [Fig. 2(d)]. We observe Au 4f_{5/2} and 4f_{7/2} XPS peaks at binding energy values of 87.0 eV and 83.3 eV, respectively, which indicates that the valence state of Au in NPGs is metallic Au(0). The deconvoluted Mo high-resolution spectrum indicates that Mo 3d_{3/2} and 3d_{5/2} peaks are present at 231.9 eV and 228.7 eV, respectively, which is indexed to Mo(IV).¹⁵ A shoulder peak is also observed right next to the Mo 3d_{5/2} peak, which can be indexed to a multiple valence

state of the S 2s peak. High resolution scan of the S 2p region reveals two different kinds of S doublets. The peaks at 163.7 eV and 162.5 eV originate from both the bridging S₂²⁻ and apical S²⁻ ligands of MoS_x, whereas the other two peaks located at 162.2 eV and 161.0 eV are indexed to the terminal S²⁻ and S₂²⁻ ligands.^{20,21} The presence of various S ligands in the molybdenum sulfide deposited on the NPG surface therefore affirms the formation of amorphous MoS_x in the photothermal deposition process.²² This result once again affirms the localized surface temperature of NPG achieving ≥ 230 °C and triggering the amorphous formation of MoS_x. Notably, we observe that all MoS_x-NPG hybrids exhibit higher bridging S₂²⁻/apical S²⁻ ligands to the terminal S²⁻ ratio (within 1.57–1.23) than pure amorphous MoS_x [(0.93, Fig. 2(e) and Fig. S5]. It has been reported that

the bridging S_2^{2-} and apical S^{2-} ligands (hereby collectively labeled “unsaturated S atoms”)⁶ are more catalytically active for HER reaction due to their more reactive undercoordinated sites that allow more efficient adsorption of hydrogen ions and faster formation of hydrogen.^{20,22–24} Thus, our overgrowth synthesis of MoS_x on NPG yields promising hybrid materials that is expected to enhance the catalytic property of both pure MoS_x and NPG. Subsequently, the composition of amorphous MoS_x on the NPG surface is analyzed using the XPS peak area ratio of Mo and S. The S/Mo atomic ratios decrease from 3.49, 3.29, 3.08, to 3.06 as the amount of MoS_x added increases from 0.5% MoS_x -NPG, 1% MoS_x -NPG, 1.5% MoS_x -NPG, to 2% MoS_x -NPG, respectively [Fig. 2(f)]. Notably, all S/Mo ratios in our MoS_x -NPG samples are higher than pure amorphous MoS_x (S/Mo ratio = 3.01), which further affirms the presence of more unsaturated S structures in our MoS_x -NPG hybrids, which are expected to enhance the electrocatalytic activities. We attribute this to the growth of MoS_x on supports made of highly conductive materials such as NPG, which results in immense chemical and electronic coupling between MoS_x and the support surface. Such an interaction also gives rise to a significant decrease in the charge transfer resistance and thus increases the number of active sites (bridging S_2^{2-} and apical S^{2-} ligands) of MoS_x .^{7,25}

We also analyze the yield of amorphous MoS_x deposition after solar simulator irradiation to demonstrate the efficiency of our photothermal decomposition method. The actual Mo ratio values, calculated using the concentrations of Mo and Au obtained from ICP-OES, are very close to the stoichiometric Mo ratio (Fig. S6), indicating the high yield of MoS_x deposited onto NPG. For 0.5% MoS_x -NPG and 1.0% MoS_x -NPG, the yields are 100%. In the case of 1.5% MoS_x -NPG and 2.0% MoS_x -NPG, the yields are as high as 94% and 95%, respectively. The slight decrease in yields can be attributed to the loading capacity of NPG, which might not be as efficient as for heavier weights of the overgrowth material. Nevertheless, the high deposition yield of >94% implies that the majority of the as-synthesized MoS_x is deposited directly onto the NPG surface and not in the bulk solution. This is because the highest localized temperature is achieved at the NPG surface, which also acts as the support base for the overgrowth. Our results clearly validate the effectiveness of our photothermal-based overgrowth method for particle hybridization.

In Sec. III, we highlight the enhanced electrocatalytic property of our hybrid MoS_x -NPG nanoparticles by hydrogen evolution reaction (HER) as a model reaction. In particular, two HER performance indicators, namely, the onset potential and Tafel slope values, are analyzed. Briefly, the hybrid nanoparticles are drop cast onto a glassy carbon working electrode and immersed in 0.5M H_2SO_4 aqueous solution using a three-electrode setup comprising of the saturated calomel electrode (SCE) and graphite rod as reference and counter electrodes, respectively. All potential values are calibrated and reported with respect to a reversible hydrogen electrode (RHE). First, linear sweep voltammetry (LSV) measurements reveal that the 0.5% MoS_x -NPG hybrid exhibits the lowest onset potential of -193 mV, whereas the onset potentials of 1% MoS_x -NPG, 1.5% MoS_x -NPG, and 2% MoS_x -NPG are -201 mV, -222 mV, and -227 mV, respectively [Fig. 3(a)]. We also notice that all MoS_x -NPG hybrids result in lower onset potentials than the control experiment using only pure amorphous MoS_x (-232 mV), which indicates that the MoS_x -NPG hybrid particles exhibit significantly enhanced

HER catalytic performance. On the other hand, we also affirm that the main catalytic material is the deposited MoS_x by comparing the HER current density per area per unit metal mass of pure MoS_x and NPG [Figs. 3(a) and 3(b)]. At -400 mV, MoS_x (1020 mA/cm² μg_{Mo}) exhibits more than 2100 times higher current density than NPG (0.47 mA/cm² μg_{Au}), which clearly illustrates that MoS_x is much more electrochemically active for HER than NPG and is the main catalytic material in the MoS_x -NPG hybrid.

In addition, we compare the Tafel slopes, an intrinsic property of electrocatalysts that reflects the overpotential required to increase the HER reaction rate by 10 times, of all our hybrid samples. The hybrid MoS_x -NPG nanoparticles exhibit a much lower Tafel slope as compared to pure amorphous MoS_x (87 mV/dec), with the lowest Tafel slope achieved by 0.5% MoS_x -NPG (50 mV/dec) [Fig. 3(c), Table S1]. This observation reaffirms the improved HER catalytic performance of the hybrid MoS_x -NPG nanoparticles compared to pure MoS_x , which also highlights the important contribution of NPG in providing high conductivity for fast charge transfer and transport.

We also exemplify the importance of our direct overgrowth hybridization process by examining the catalytic performance of our hybrid particles as compared to the physically mixed mixture of NPG with prefabricated 0.5% amorphous MoS_x . We show that our 0.5% MoS_x -NPG hybrid achieves 60 mV lower onset potential and 40% lower Tafel slope compared to the physically mixed control sample [onset potential of -294 mV, Tafel slope of 73 mV/dec, Figs. 3(a) and 3(c)]. Thus, it is evident that hybrid MoS_x -NPG particles produced using our photothermal overgrowth technique exhibit superior HER catalytic activity over physically mixed composites. This highlights the synergistic effect arising from the particle-level hybridization of the two materials. In addition to the enhanced electrocatalytic ability, we also showcase the stability of the HER performance of MoS_x -NPG hybrids by showing near negligible current decay in the time-dependent current density curve at -225 mV after 8 h [Fig. 3(d)]. Overall, our collective results of low onset potentials/overpotentials, small Tafel slopes, and current stability clearly demonstrate that the hybrid MoS_x -NPG particles produced via our photothermal overgrowth technique exhibit significantly enhanced electrocatalytic property that boost the HER efficiency.

The origin of the enhanced catalytic effect exhibited by our hybrid nanoparticles can be elucidated by the XPS peak ratio between the unsaturated S and the terminal S for each hybrid nanoparticle [Fig. 2(e)]. As mentioned above, we attribute the main reason for the enhanced catalytic activity to the higher percentage of the highly reactive and undercoordinated bridging S_2^{2-} and apical S^{2-} ligands in the hybrid nanoparticles. 0.5% MoS_x -NPG hybrid nanoparticles possessing the highest proportion of catalytically active unsaturated S ligands exhibit the highest HER activity. As the ratio between unsaturated S and terminal S decreases from 1.5 to 1.2 with an increase in MoS_x from 0.5% to 2% , HER activity becomes poorer. Besides, pure amorphous MoS_x exhibits the lowest catalytic activity because its unsaturated S/terminal S ratio is below 1 . Hence, this observation reaffirms that the enhanced electrocatalytic property of our hybrid MoS_x -NPG nanoparticles arises from the increased unsaturated S atoms with highly active undercoordinated sites.

FIG. 3. Catalytic activity of MoS_x-NPG in hydrogen evolution reaction. (a) Linear sweep voltammetry (LSV) polarization curves of MoS_x-based samples with and without NPG, at a scan rate of 2 mV/s, electrolyte solution: 0.5M H₂SO₄ aqueous solution saturated with Ar. (b) LSV polarization curve of NPG under the same experimental conditions. (c) Corresponding Tafel plots derived from the samples in (a). (d) Chronoamperometric curve for 0.5% MoS_x-NPG. (e) (i) Electrochemical impedance spectroscopy (EIS) Nyquist plots of different samples and the corresponding equivalent circuit model for simulation. (ii) Magnified image of the green rectangular region in (i).

We further examine the role of NPG as a cocatalyst in the hybrid systems by measuring the electrical conductivity with electrochemical impedance spectroscopy (EIS). EIS results reveal that the radius of the semicircle is dramatically reduced when amorphous MoS_x is hybridized with NPGs [Fig. 3(e)]. By simulating the Nyquist plots using the circuit model, the charge-transfer resistance of 0.5%MoS_x-NPG (29.6 Ω) is merely ~10% of amorphous MoS_x (313 Ω). Similarly, all other MoS_x-NPG hybrids exhibit much lower charge-transfer resistance than amorphous MoS_x (32.2–37.8 Ω). It is well known that although amorphous MoS_x possess abundant active sites, the poor conductivity of amorphous MoS_x restricts its application in electrochemical catalysis.^{19,26,27} Hence, we postulate that the presence of the highly conductive NPG dramatically improves the conductivity of the hybrid nanoparticles, which in turn improves the electrochemical activity of the nanoparticles. Therefore, based

on these collective results, we envisage that the increased presence of unsaturated S atoms and enhanced conductivity synergistically contribute to the boosted HER activity in the MoS_x-NPG hybrid, making them a promising material to be applied in reactions and catalysis in various fields.

III. CONCLUSION

In summary, we have successfully demonstrated the solution-based, SPR-mediated photothermal hybridization of MoS_x and NPG to form colloidal MoS_x-NPG hybrids without the need for bulk heating. Notably, the amount and thickness of amorphous MoS_x on NPG can be tuned by changing the initial concentrations of the precursors. We also demonstrate the potential application of

NPG-based hybrid materials by employing the MoS_x-NPG hybrids as an enhanced electrocatalyst for HER reaction. Our MoS_x-NPG hybrids exhibit much lower onset potential (−193 to −227 mV) and smaller Tafel slope values (50–68 mV/dec) than pure amorphous MoS_x (−232 mV, 87 mV/dec). The enhanced catalytic activity of MoS_x-NPG hybrids is attributed to the abundance of unsaturated S active sites and better conductivity in the presence of the NPG cocatalyst platform. This work offers a new synthesis strategy for the preparation of an energy conversion functional hybrid by utilizing the photothermal effect of NPG. Notably, our new strategy features a low cost synthesis technique under mild ambient conditions, which produces high quality hybrid nanoparticles with abundant active sites for various applications in the fields of reaction, catalysis, and energy.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for experimental methods and supporting figures and discussion.

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