Silver nanoparticle array on weakly interacting epitaxial graphene substrate as catalyst for hydrogen evolution reaction under neutral conditions

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ABSTRACT

The paucity of research on hydrogen evolution reaction (HER) under neutral conditions, which is a more sustainable way to produce H2 compared to acidic and alkaline HER, encourages the development of efficient catalytic materials and devices and deeper investigation of the mechanisms behind neutral HER. We present an electrode concept for facilitating HER under neutral conditions. The concept entails the use of annealing-reshaped silver (Ag) nanoparticle array on monolayer epitaxial graphene (MEG) on 4H-SiC. Measurements of HER performance show more positive onset potential of the cathodic HER for Ag-decorated MEG compared to that for pristine MEG, indicating improved water dissociation at Ag/MEG electrodes. Complementary morphological characterization, absorption measurements, and Raman mapping analysis enable us to ascribe the enhanced catalytic performance of electrodes decorated with 2 nm thick annealed Ag on the synergetic effect originating from simultaneous water reduction on circular Ag nanoparticles of 31 nm in diameter and on compressively strained Ag-free graphene regions. The overall results pave the way toward development of stable van der Waals heterostructure electrodes with a tunable metal–carbon interaction for fast HER under neutral conditions.

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Innovative hydrogen production technologies are currently at the forefront of scientific efforts to decrease dependence on conventional energy sources like non-renewable and exhaustible fossil fuels and to boost next-generation green energy technologies.1,2 In light of this trend, electrochemical processes behind water splitting have been broadly regarded as the most promising and cost-effective approach for sustainable production of hydrogen with zero carbon emission.3,4 However, the most efficient electrocatalysts are based on critically raw materials, namely, bulk Pt group metals (PGMs), which is the major deterrent toward widespread use of H2O electrocatalysis for large-scale H2 production. Furthermore, high-efficiency hydrogen evolution reaction (HER) typically proceeds under extreme pH conditions (in acidic and/or alkaline electrolytes), which has its own drawbacks related to unavoidable corrosion of the electrolyzers in acidic environment and use of highly cost anion exchange membranes for alkaline HER.5 In contrast, less investigated and understood HER under neutral conditions is more sustainable and environmentally...
friendly way to produce molecular hydrogen.\textsuperscript{6} This has prompted a global search for bulk PGM-free electrocatalysts for neutral HER.\textsuperscript{7–8}

During the last decade, graphene-supported metal carbides,\textsuperscript{9} disulfides,\textsuperscript{10} phosphides,\textsuperscript{11} selenides,\textsuperscript{12} oxides,\textsuperscript{11–12} and nitrides\textsuperscript{13} have gained significant attention as appealing materials beyond PGM electrocatalysts. Apart from these studies, there are several reports on using metal nanoparticle (NP) decoration to enhance the HER activity of CVD graphene\textsuperscript{1} transferred to Si/SiO\textsubscript{2} wafer and reduced graphene oxide.\textsuperscript{14–15} A major advantage of such systems lies in the fact that each metal nanoparticle on graphene may serve as a separate nanoelectrode, providing abundant catalytic active sites. Furthermore, since metal nanoparticles (especially silver) are plasmonically active, they can help to boost not only the efficiency of electronic and optoelectronic devices\textsuperscript{16–19} but also the HER performance through surface plasmon-driven electrochemical reduction of water.\textsuperscript{20–23} This makes that graphene supported noble metal NPs excellent candidates for realization of new electrocatalyst designs.

Here, we study HER performance of Ag nanoparticle-decorated monolayer epitaxial graphene (MEG) on SiC under neutral environment. As one of the most prominent graphene family representatives, epitaxial graphene has all key attributes of free-standing graphene (FGS) but exhibits higher reactivity compared to FSG, which originates from substrate-induced n-doping and compressive strain of the SiC-supported graphene layer.\textsuperscript{24–25} The enhanced binding affinity of epitaxial graphene to external adsorbates may trigger the formation of a larger number of stable early stage nuclei (compared to FSG) during metal deposition, making the growth process controllable (tunable morphology of NPs over a wider range) from the technological point of view.

By performing high-temperature thermal decomposition of nominally on-axis 4H-SiC (0001) bulk substrates in Ar atmosphere, we initially synthesized large-area monolayer epitaxial graphene. It is important to note that the graphene formation is a complex process that comprises a series of stages [Si–C bond breaking, Si sublimation, (6,3 × 6,3)R30° surface reconstruction, re-arrangement of sp\textsuperscript{2}-bonded carbon atoms in 2D honeycomb structure] and requires a strict control of the growth conditions in an inductively heated reactor at each growth stage.\textsuperscript{26} Despite its complexity, this process allows us to achieve a complete coverage of the 4H-SiC surface with monolayer graphene. The high quality of as-grown MEG was then confirmed by Raman mapping analysis and optical reflectance mapping (further details are provided in supplementary material, Sec. S1, Figs. S1 and S2). MEG electrodes were then modified in a following way:

1. Surface metallization of MEG through direct current (dc) magnetron sputtering of pure Ag target (purity 99.999%) in argon (Ar) atmosphere at room temperature. More details on the growth process can be found in our previous work.\textsuperscript{25} We synthesized two types of Ag films: discontinuous films (nominal film thickness 2 nm) featuring isolated nanoscale islands and percolated films with nominal thickness of 10 nm. However, thicker silver films were also explored.

2. Thermal annealing at 260 °C in an Ar atmosphere for 1 h to reshape the as-grown Ag nanostructures, to eliminate incomplete coalesced clusters, and to eventually increase the island size. The details of the morphology studies are included in supplementary material (Sec. S2), while the schematics of the formation process of Ag nanoparticles is shown in Fig. S3 (supplementary material).

The resulting morphologies for 2 and 10 nm films are shown in Figs. 1 and 2, respectively. As was confirmed by x-ray diffractometry (XRD) analysis, both films have the face centered cubic (fcc) crystal structure (Fig. S4, supplementary material). At a nominal thickness of 2 nm, we observe the formation of island-like film [Fig. 1(a)], as evidenced by the presence of small, separated nanoislands (with mean particle diameter \(\mu \approx 15\) nm) with no evident interconnections between them. The corresponding Ag particle diameter distribution is plotted in Fig. 1(c). It is worth noting that the formed nanoislands uniformly cover the MEG surface with average density of \(1.6 \times 10^{13}\) cm\(^{-2}\). The role of the MEG substrate in the initial formation of isolated nanoscale islands is described in the supplementary material (Sec. S3). Shape analysis of the Ag islands using two shape descriptors— in-plane aspect ratio \(\frac{\text{major axis length}}{\text{minor axis length}}\) and circularity \(\frac{4\pi \text{Area}}{\text{Perimeter}^2}\)—also suggests that the as-grown Ag islands are mostly non-spherical or even irregularly shaped (Fig. S5, the supplementary material). More specifically, a large variability in both parameters, which are far from the value of 1 corresponding to spherical shapes, is observed, indicating incomplete coalescence. As clearly seen in the SEM image [Fig. 1(b)] and the corresponding particle size distribution histogram [Fig. 1(d)], the annealing of the sample at 260 °C in an Ar atmosphere for 1 h leads to a twofold increase in particle size (from \(\sim 15\) to \(\sim 30\) nm) and island density decrement from \(1.6 \times 10^{11}\) to \(3.2 \times 10^{10}\) cm\(^{-2}\). The thermal annealing enhances surface diffusion such that relatively small cluster impinge on and get incorporated into the larger ones. Additionally, a dissociation of small clusters at the expense of large ones (Ostwald ripening) may occur. Both these processes favor cluster size increase, while the existing material is redistributed into fewer islands.\textsuperscript{25} Furthermore, we notice a substantial change in the shape of Ag nanoparticles after annealing: from irregularly shaped three-dimensional islands to flat right cylinders with nearly circular cross sections [inset in Fig. 1(b)]. The shape analysis corroborates this observation, demonstrating that both the aspect ratio and the circularity approach a value of 1 for an ideal circle (Fig. S5, the supplementary material). The spherical shape of Ag islands is explained by the fact that with the increasing temperature, incomplete coalesced island clusters résumé reshaping (including grain boundary migration) leading to close-to-equilibrium shapes (e.g., hemispheres). Another aspect is that facets disappear as the increase in temperature leads to larger kink density on the surface of the islands.\textsuperscript{25}

Next, we find that the morphology of the Ag films is very sensitive to the modification of the deposited Ag amount. As can be seen from Fig. 2(a) (see also data shown by Figs. S6 and S7 for 15 and 30 nm-thick Ag films on MEG, the supplementary material), 10 nm-thick Ag on MEG shows percolated structure, which is randomly formed due to impingement and incomplete coalescence of initially separated Ag nanoislands during the growth process. In this case, approximately 62% of MEG surface is densely covered with interconnected Ag nanostructures. After annealing, the 10 nm-thick percolated nanostructures develop into Ag droplet-like structures, as shown in Fig. 2(b). Moreover, the average particle diameter is found to be \(\sim 73\) nm [see the inset in Fig. 2(b)] and the coverage area is decreased to 37%. Meanwhile, the nanoisland density is only \(7.6 \times 10^6\) cm\(^{-2}\),
which is much lower than that for the annealed 2 nm-thick Ag sample. The results of morphological analysis for both considered samples before and after annealing are summarized in Table I. Based on the morphological analysis, one can conclude that the 2 nm silver layers grow according to Volmer–Weber growth scheme, forming 3D islands initially. With the increasing Ag coverage, the 3D islands begin to coalesce and form a metastable percolated network, which tends to equilibrate via thermally activated formation of the completely discontinuous Ag nanofilm consisting of large Ag nanoislands. The fact that Ag coverage area is significantly decreased after annealing points out the pronounced de-wetting of the Ag film on MEG. The main precondition for observation of such growth kinetics is the predominance of the binding energy between Ag adatoms over the interaction energy between Ag adatoms and MEG surface.

The modified epitaxial graphene electrodes were further studied with regard to their HER catalytic activity under neutral environment. (A more detailed description of the HER study is presented in the supplementary material, Sec. S4; Fig. S8.) It is worth noting that HER...
under neutral conditions is a quite complicated process,\(^5\) which involves reduction (Volmer step) of both hydronium (H\(_3\)O\(^+\)) ions (at low overpotentials close to 0 V vs \(V_{\text{RHE}}\)) and H\(_2\)O molecules (at higher overpotentials),

\[
\begin{align*}
H_3O^+ + e^- + ^* & = H^+ + H_2O \quad \text{(Volmer),} \\
H_2O + e^- + ^* & = H^+ + OH^- \quad \text{(Volmer),}
\end{align*}
\]

where \(^*\) corresponds to the active catalytic sites at MEG or Ag-decorated MEG electrode surface and H\(^+\) refers to the adsorbed hydrogen atom. A subsequent molecular hydrogen formation occurs then via Heyrovsky or Tafel pathways.\(^5\) Figure 3(a) shows the current density–potential (\(j–V\)) measurements at a scan rate of 30 mV/s. Unmodified pristine epitaxial graphene electrode exhibits large onset potential at \(-0.884 \text{ V}_{\text{RHE}}\) to drive a current density of \(-0.10 \text{ mA/cm}^2\) for direct water reduction, which is the rate-determining step.\(^34\) This suggests a poor electrocatalytic activity of pristine MEG toward the HER, probably due to low mobility of H\(^+\) on MEG.\(^35\) It is likely that the nominal activity of MEG can be explained by the unique surface topology of the electrode, including step-terraced morphology, the presence of nanosized bilayer inclusions with highly reactive edges and strain-doping fluctuations. Concomitantly, a modification of the MEG electrode through subsequent deposition and annealing of Ag films gives rise to enhancement of the HER activity of the electrode. A 10 nm-Ag/MEG electrode shows more positive onset-potential at \(-0.428 \text{ V}_{\text{RHE}}\) than that of 2 nm-Ag/MEG and MEG electrodes (\(-0.743 \text{ and } -0.884 \text{ V}_{\text{RHE}}\)) with smaller overpotentials to drive a current density of \(-0.10 \text{ mA/cm}^2\). By comparing the two modified

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area of coverage, %</th>
<th>Island density, particle/cm(^2)</th>
<th>Mean particle area, nm(^2)</th>
<th>Mean particle diameter, nm</th>
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<td>(1.6 \times 10^{11})</td>
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<td></td>
<td>Annealed</td>
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<td>(3.2 \times 10^{10})</td>
<td>853.04</td>
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<tr>
<td>10 nm Ag</td>
<td>As-grown</td>
<td>62.42</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
</tr>
<tr>
<td></td>
<td>Annealed</td>
<td>37.41</td>
<td>(7.6 \times 10^{8})</td>
<td>4662.73</td>
</tr>
</tbody>
</table>

**Table I.** The results of morphological analysis of 2 and 10 nm-thick silver films onto monolayer epitaxial graphene before and after annealing.

**FIG. 3.** (a) \(j–V\) curves of the epitaxial graphene/4H-SiC, annealed 2 nm-Ag/MEG, and annealed 10 nm-Ag/MEG electrodes in the 0.5 M Na\(_2\)SO\(_4\) solution under chopped AM1.5G 100 mW/cm\(^2\) illumination, at a scan rate of 30 mV/s. (b) Corresponding Tafel plots for HER in neutral medium. (c) The proposed mechanism of the hydrogen evolution reaction at the annealed 2 nm-Ag decorated MEG electrode under neutral conditions. Based on the analysis of the experimental data, one can conclude that the HER at the annealed 2 nm-Ag/MEG electrode immersed in unbuffered medium proceeds through the Volmer–Heyrovsky mechanism, which is in line with literature data.\(^37\)
electrodes, we cannot ascribe the positive shift of the on-set potential (observed for 10 nm-Ag/MEG) to the increase in HER performance. Instead, this shift can be attributed to the mass transport effect. As can be seen from Table I, the total coverage of 10 nm-Ag nanoparticle arrays on MEG is larger than that of 2 nm-Ag nanoparticle arrays on MEG, which makes diffusional behavior at the 10 nm-Ag/MEG electrode closer to that of the bulk silver case, causing an overpotential decrease. In other words, diffusion is more planar and less locally convergent in the case of a 10 nm-Ag/MEG electrode. From Fig. 3(a), the intersection of the j–V curves of the two modified electrodes at the potential of −1.03 V RHE can also be identified. Compared to the 10 nm-Ag/MEG electrode, a 2 nm-Ag/MEG electrode starts to require a smaller overpotential for driving a current density beyond −1.2 mA/cm². The analysis of Tafel plots confirms that a 2 nm-Ag/MEG electrode has the highest electrochemical activity for H₂-evolution reaction with the smallest slope of 282 mV/dec [Fig. 3(b)], which is comparable to the values of Tafel slope of selected metals (especially palladium) for HER at low concentration of hydronium ions. However, it is still larger than Tafel slope of the state-of-the-art 20 wt. % Pt/C electrode in 0.5 M Na₂SO₄ (132.8 mV/dec). This indicates that proper electrode design strategy should be applied to minimize the overpotential and reduce the Tafel slope. Schematic illustration of the mechanism behind hydrogen evolution reaction at the annealed 2 nm-Ag/MEG electrode is given in Fig. 3(c).

In the case of unbuffered electrolyte used, the concentration of hydronium ions H₃O⁺ or other proton donors is exceedingly low. Therefore, the reduction current does not depend on the proton mass transport. Only a current arising from direct reduction of water contributes to the j–V profile. As a result of the absence of the mass transport limitation, no significant mismatch between pH near Ag/MEG electrode surface and the bulk electrolyte is anticipated. Otherwise, we should have seen the plateau current related to mass transport limitation of protons, rather than only current attributed to direct water reduction, as in our case.

The stability of the proposed electrodes during HER was also investigated. As shown in Fig. S9 (the supplementary material), the electrocatalytic current of MEG electrode was significantly decreased after ten times measurements, indicating that the 4H-SiC electrode has higher HER activity and side reaction of forming SiO₂ layer, after ten times measurements, indicating that the 4H-SiC electrode was significantly decreased. In contrast, our strategy implies using of unbuffered electrolyte (0.5 M Na₂SO₄), which provides more favorable conditions (reaction environment) for real water splitting (including seawater splitting). Consequently, the Ag electrode surface and the bulk electrolyte is anticipated. Otherwise, we should have seen the plateau current related to mass transport limitation of protons, rather than only current attributed to direct water reduction, as in our case. As expected, an overall increase in the absorbance is observed when the sputtered Ag thickness increases. It is clearly seen that the intensity of the localized surface plasmon resonance (LSPR) peak of 2 nm-thick Ag increases after annealing at 260 °C, while the LSPR peak position does not change. On the other hand, the annealing of a 10 nm-thick Ag sample at 260 °C followed by transition from percolated morphology to island-like morphology (with a particle diameter of 73 nm) results in substantial redshift of the LSPR peak (31 nm) and enhancement of the LSPR peak intensity. Such a substantial redshift of LSPR may originate from the cumulative effect of the particle size increase due to thermal annealing and of change in the free electron density of the metallic nanostructures due to a charge transfer from metal to graphene. Judging from these results, scenario (iii) can be ruled out as a possible reason for the HER performance enhancement. This is because the annealed 10 nm-Ag/MEG sample exhibits stronger LSPR peak compared to the annealed 2 nm-Ag/MEG. This means that the effect of hot electrons on the electrochemical reduction of water would be more pronounced for the annealed 10 nm-Ag/MEG electrode, which is not the case. In line with this, no plasmonic hot electron induced photocurrent response is detected for both modified electrodes, which is probably due to a limited transfer of hot electrons from metal to graphene.

To investigate the possible charge transfer between silver and epitaxial graphene, Raman mapping analysis of Ag-decorated MEG samples has been performed before and after annealing (supplementary material, Sec. S5). Nominally island-like morphology of the as-grown 2 nm-Ag nanofilm results in large-area uniform n-type doping of monolayer graphene (with a mean carrier density of 9.5 × 10¹⁵ cm⁻²)
due to the charge transfer from Ag to MEG. This is evidenced by the very narrow spread of the data points (marked by empty magenta rhombi) in the doping-affected region of 2D–G space [see Fig. 5(a)]. In contrast, the annealed 2 nm-Ag film exhibits completely different picture of the mutual dependence between 2D and G peak positions. We notice that the corresponding data points (filled green squares) move into the so-called forbidden area of 2D–G space and scatter on the left side of the strain line, suggesting a decrease in electron doping (charge transfer from Ag to MEG) and an appearance of large non-uniform compressive strain due to annealing-induced de-wetting and coarsening of the Ag nanoislands. Interestingly, the 10 nm-Ag/MEG sample before and after annealing demonstrates remarkably similar 2D–G dependencies unlike the annealed 2 nm-Ag/MEG sample, which suggests a weakened charge transfer related doping of MEG. This could also explain the higher HER activity of 2 nm-Ag/MEG. It is most likely that only exceedingly small sub-nanometer Ag clusters (with unpaired electrons) can effectively dope the monolayer epitaxial graphene, while the formation of large islands leads to reduced Ag/MEG interaction that limits the charge transfer from Ag to MEG.

Furthermore, additionally to an obvious nanoisland coarsening, the de-wetting process also reduces the overall Ag-MEG contact area, as shown by SEM, thereby enlarging the area of deposit-free graphene regions with intrinsic carrier density affected only by SiC-related charge transfer.

From Figs. 5(b) and 5(c), it is seen that the graphene covered with 2 nm-Ag experiences larger compressive strain after annealing compared to the annealed 10 nm-Ag/MEG sample. It is interesting to note that the interaction strength between water molecules and graphene surface can be modulated by strain. It has been shown that
the compressive strain leads to an increase in both binding energy of water molecule and charge transfer between graphene and water. Therefore, it is reasonable to assume that the enhanced HER performance of the annealed 2 nm-Ag/MEG electrode is originating from the synergy of electrochemical processes on the Ag islands with relatively strong binding affinity to MEG and on compressively strained graphene regions, respectively [see also Fig. 3(c)].

In summary, the electrode design for hydrogen evolution reaction in neutral environment was developed through integration of annealing-reshaped magnetron-sputtered Ag nanoparticle array and weakly interacting epitaxial graphene on 4H-SiC. By performing morphology analysis, electrochemical studies, UV-vis absorption measurements, and Raman mapping analysis, a fundamental understanding of the nature of the annealing effect on the physical properties of Ag-modified electrodes and the mechanisms underlying hydrogen evolution reaction under neutral pH conditions was gained. Improved catalytic performance of annealed 2 nm-Ag/MEG electrode as compared to thicker Ag films, confirmed by smaller Tafel slope, has been explained by a combined effect of two competing mechanisms: (i) water reduction process on small circular Ag nanoislands, which are relatively strongly coupled to graphene, favoring faster interfacial charge transfer and (ii) water reduction process on compressively strained Ag-free graphene regions with high enough binding affinity and catalytic efficiency with respect to water molecules. More rational design of the Ag/MEG electrode through realization of precise control of Ag–MEG interaction strength and nanoparticle array architecture will provide useful prerequisites of elaborating reliable technology of van der Waals heterostructure electrodes for fast and sustainable HER under neutral conditions.

See the supplementary material for the results of the shape analysis and Raman studies of Ag-decorated epitaxial graphene before and after thermal annealing. The description of the formation of Ag nanoparticles on MEG and electrochemical experiment is also contained in the supplementary material.

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AUTHOR DECLARATIONS

Conflict of Interest

There are no conflicts to declare.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES


