Ligand-Exchange-Assisted Layer-by-Layer Assembly of Au–Pt Bimetallic Nanocomposite Films and Their Electrocatalytic Activities for Hydrogen Evolution Reaction

Sujin Lee, Yongkwon Song, Jinhan Cho, Youn Jeong Jang,* and Bongjun Yeom*

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ABSTRACT: Platinum (Pt) is a popular electrocatalyst for the hydrogen evolution reaction (HER) for water splitting. However, a facile synthesis route with improved activity and stability remains to be established. In this study, Au–Pt bimetallic nanocomposite electrodes for the HER are prepared by ligand-exchange-assisted layer-by-layer (LbL) self-assembly methods. Pt and Au nanoparticles (NPs) are alternately deposited onto Ti electrodes paired with short alkyl amines. This process is accompanied by the removal of the preattached bulky surface ligands. The resulting Pt and Au NP LbL nanocomposite films are characterized by uniform thin-film depositions with high electrical conductivity (8.7×10^4 S cm⁻¹). With the increase in the number of depositions, the overpotentials of the Au–Pt LbL samples gradually decrease and reach 66 mV at a current density of 10 mA cm⁻² under an acidic condition of 0.5 M H₂SO₄, which is accomplished with a significantly small Pt loading (0.73 wt %). Furthermore, the overpotentials of the Au–Pt bimetallic LbL films are one-third of the Pt NP LbL films. The enhanced activity can be attributed to the synergistic effect of the *d*-band shift



from the bimetallic heterostructure, high electrical conductivity, rapid charge transfer, and increased electrochemical surface area. **KEYWORDS**: water splitting, hydrogen evolution reaction, layer-by-layer assembly, Au-Pt bimetallic film, electrocatalyst

1. INTRODUCTION

Electrochemical water splitting is a promising technique for producing hydrogen as a carbon-neutral energy resource.^{1,2} Among various electrocatalysts for water reduction, platinum (Pt) is a popular choice as the moderate Pt-H bond strength is optimal for hydrogen adsorption and desorption, as indicated by volcano plots.³ However, pure Pt exhibits several disadvantages, such as limited activity, high cost, surface poisoning tendencies, and low stability.^{1,4,5} Therefore, several researchers have attempted to enhance the activity and stability of Pt-containing catalysts. For example, bimetallic catalysts with transition metals (Cr, Mn, Fe, Co, Ni, Cu, and Zn) or noble metals (Ru, Pd, Ag, and Au) have been used to harness their electronic and bifunctional effects.^{3,4,6,7} Among such frameworks, Au-Pt bimetallic electrocatalysts have been reported to exhibit enhanced stability and activity. The addition of Au endows bimetallic catalysts with several advantages, such as decreased *d*-orbital vacancy of Pt for the modification of the adsorption energy of reactants,⁸ increased Pt oxidation potential for long-term stability,9 and enhanced electron transfer.¹⁰ Various synthetic approaches such as seeded growth,^{11,12} galvanostatic deposition,¹³⁻¹⁵ surface dealloying,^{16–18} and electrodeposition^{19–21} have been utilized to prepare alloys, heterostructures, and core-shell bimetallic catalysts. Nevertheless, a facile and straightforward synthesis

method remains to be established to realize large-area production and enhanced catalytic activities.

The layer-by-layer (LbL) self-assembly method has been used to fabricate uniform functional thin films onto substrates.^{22,23} Moreover, various types of wet-synthesized nanoparticles (NPs), such as Au, Pd, Pt, TiO₂, ZnO, CdSe, Fe₃O₄, and MnO, have been introduced in LbL self-assembled thin films for electrical and catalytic applications.^{24,25} The variety of surface ligands attached to the NP surfaces provide strong intermolecular interactions to generate adsorption driving forces through electrostatic interactions, hydrogen bonds, and other chemical bonds.² Recently, the ligandexchange-assisted LbL assembly technique was used to prepare highly conductive metallic NP thin films with electrical conductivities higher than 10⁴ S cm⁻¹, which is similar to the bulk metal conductivity.^{26,27} In typical preparations, after the adsorption of NPs onto the substrates, the preattached bulky surface ligands are exchanged with short-length ligands with

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Figure 1. Schematic of the preparation of Au–Pt NP nanocomposite films by ligand-exchange-assisted LbL self-assembly. Size of the illustrated objects is not drawn in scale. The FE-SEM in-plane image of the $(DETA/AuNP/DETA/PtNP)_{10}$ sample is shown in the right-bottom corner. The inset shows a cross-section of the sample.

multifunctional groups. This ligand exchange decreases the amount of insulating organic components, followed by metallic fusion between metallic NPs,²⁸ which enhances the electrical conductivities. This approach has been used to prepare various types of conductive electrodes in energy storage and conversion devices.^{27,29} However, Pt-based bimetallic nano-composite films prepared by ligand-exchange LbL assembly have not yet been reported for the hydrogen evolution reaction (HER).

Considering these aspects, in this study, Au-Pt bimetallic nanocomposite electrocatalyst thin films were fabricated by ligand exchange-assisted LbL assembly for HER reaction. Au and Pt NPs stabilized by tetraoctylammonium (TOA) ligands were assembled in alternating order, paired with small molecular linkers of diethylenetriamine (DETA) as LbL assembly partners. The resulting Au-Pt LbL electrocatalytic nanocomposite films were uniformly deposited over the substrates with high electrical conductivity (8.7 \times 10⁴ S cm⁻¹), similar to that of bulk Pt (9.4 \times 10⁴ S cm⁻¹), via interfacial infusion between the NPs facilitated by the ligand exchange LbL assembly. The best-performing Au-Pt LbL sample with a thickness of ~90 nm had a Pt loading of only 0.73 wt % and exhibited an overpotential of 80 mV at a current density of 10 mA cm⁻² under an acidic condition of 0.5 M H_2SO_4 . In comparison, the Pt sputtered film with a similar thickness demonstrated an overpotential of 62 mV. The Au-Pt LbL sample with a small Pt loading achieved a comparable overpotential (less than 100 mV), which is suggestive of enhanced catalytic activity for a given loading of the active element (Pt). Furthermore, the overpotential of the Au-Pt bimetallic LbL film was two times smaller than that of the Pt NP LbL film, despite the Pt content being 25% lower than that

of the counterpart. The enhanced performance can be attributed to the synergistic effects of uniform bimetallic heterostructures for *d*-band shift of active element of Pt lowering binding strength of protons, superb electrical conductivity, rapid charge transfer, and increased electrochemical surface area from the nanotextures of the ligand exchange-assisted LbL assembled films.

Our synthesis approach is original and the first trial for the synthesis of Au and Pt NP composite films by ligand exchangeassisted LbL assembly, best to our knowledge. Ligand exchange processes involved in each LbL assembly step have a crucial role in removal of preattached bulky organic ligands, which are insulating and electrochemically nonactive that could deteriorate electrocatalytic activities. This unique feature could contribute to enhancements in electrical conduction and charge transfer for the Au-Pt LbL samples. These characteristics combined with other advantages could show synergistic effects. Bimetallic heterostructures can be attributed to d-band shift of active element of Pt lowering binding strength of protons, and the nanotextures of the NP composite films can increase electrochemical surface area. As a result, electrocatalytic activities could be enhanced even with very small amounts of Pt loadings. Overall ligand exchange-assisted LbL assembly can be utilized in the large-area fabrication of multicomponent catalytic electrodes from various types of wetsynthesized NPs.²⁶

2. RESULTS AND DISCUSSION

Au-Pt LbL nanocomposite films were deposited onto substrates through the ligand exchange-assisted LbL assembly method (Figure 1). Spherical Au and Pt NPs were synthesized at room temperature from $HAuCl_4$ and H_2PtCl_6 aqueous



Figure 2. FE-SEM in-plane images of (a) AuPt1, (b) AuPt3, (c) AuPt5, (d) AuPt10, and (e) AuPt15 samples. (f) UV-vis absorbance spectra of $(DETA/AuNP/DETA/PtNP)_n$ samples. (g) LSV polarization curves for AuPtn samples and Pt sputtered onto Ti in 0.5 M H₂SO₄. (h) Overpotentials corresponding to the curves shown in (g) at 10 mA cm⁻¹.

precursors, respectively, mixed with an immiscible solvent of toluene and surface stabilizer, i.e., tetraoctylammonium bromide (TOABr).^{30–32} After adding NaBH₄ as the reducing agent, the phase-transferred NPs were washed and redispersed in toluene and then used for LbL-assembly (details are provided in the Experimental Section). The diameters of Au and Pt NPs were 5.8 \pm 0.1 and 2.9 \pm 0.1 nm, respectively (Figure S1). After depositing the prelayers of polyethylenimine (PEI), TOA-stabilized Au NPs were deposited onto the surfaces. Subsequently, a ligand exchange reaction was implemented, in which the TOA ligands attached to the NP surfaces were replaced with DETA with higher binding energies.²⁷ Then, the next layer of NPs was adsorbed onto the surfaces. During the NP depositions, the bulky surface ligands of TOA were removed, and metal surfaces could directly bind to the preadsorbed DETA owing to the high affinity between the amine-functionalized ligand and NPs.³ These processes were repeated until the desired number of depositions was achieved. To prepare typical Au and Pt nanocomposite LbL films, Au and Pt NPs were alternately deposited with DETA as the exchange ligand, producing $(DETA/AuNP/DETA/PtNP)_n$ samples, where *n* indicates the number of repetitions. Note that in this paper the notation AuPtn is used to represent the nanocomposite films, and Aun and Ptn indicate the control samples prepared with single NPs and DETA with compositions of $(DETA/Au)_n$ and $(DETA/Au)_n$ $Pt)_{n}$ respectively. For the comparative investigations among these samples, the numbers of total NP layers were matched as described in the subsequent sections. Typically, AuPt10 samples were compared with the Au20 and Pt20 samples. The field emission scanning electron microscopy (FE-SEM) image in Figure 1 shows the uniform deposition of NPs for the ~60 nm thick AuPt10 sample (inset).

The FE-SEM images of the AuPt samples show random aggregations of the adsorbed NPs without spatial order (Figure 2a-e), similar to the previous reports with the LbL preparation method.^{2,34} As the number of paired depositions (*n*) increased from 1 to 10, the grain size of the NP aggregates and their

surface coverage gradually increased, and nearly full coverage was achieved over the Ti substrates for the AuPt10 sample. In addition, cross-sectional SEM images of the AuPtn samples showed gradual increase in thickness, reaching to ~60 nm of thickness for the AuPt10 sample with rough surfaces by aggregations of NPs (Figure S2). These deposition morphologies and behaviors are similar to those observed for typical LbL-assembled samples prepared with NPs.^{28,35} In order to investigate deposition behaviors for each LbL cycle, UV-vis measurements were performed after each layer deposition for the AuPt sample up to n = 5 (Figure 2f). The measurements of n > 5 were omitted to reduce redundancy of the repeated measurements. The absorbance intensities monotonically increased with the increase in the number of depositions. A localized surface plasmonic band from AuNP at 576 nm (Figure S3) was observed for AuPt0.5, where n = 0.5 indicates half deposition of the repetitive layer, generating a pair of DETA/AuNP. Further deposition of DETA/PtNP led to a slight increase in the absorbance intensity for the entire wavelength region with a slight red-shift. With the increase in the number of depositions, red-shifting and broadening of the plasmonic bands were observed owing to the collective coupling of the Au and Pt plasmonic bands by the dense depositions.^{28,33} These deposition behaviors are similar to typical observations for the LbL assembly preparations,²⁸ which is consistent with gradual increases in the adsorbed amounts of NPs observed in the FE-SEM analysis. The small increase in the absorbance intensities for the PtNP deposition can be attributed to the low Pt loading, as discussed in the following section. Notably, the absorbance peaks from DETA were difficult to identify because of overlaps with the Pt NP peaks (Figure S3b,c).

During LbL assembly, the preattached TOA ligands were replaced with the short-length ligands of DETA as observed in other works utilizing ligand exchange-assisted LbL assembly.^{23,26–29} FTIR spectroscopy in the attenuated total reflection (ATR) mode was performed to observe the ligand exchange processes (Figure S4). The C–H stretching peak



Figure 3. TEM and EDX analysis results for the AuPt NP nanocomposite films: (a) Electron image and EDX mapping images of (b) overlapped Au and Pt, (c) Au, and (d) Pt for the AuPt10 sample. (e,f) HR-TEM images of the AuPt10 sample. (g) SAED pattern for the AuPt10 sample. Yellow and red half circles indicate Au and Pt reflections, respectively.

intensities at $2850-2950 \text{ cm}^{-1}$ from the preattached ligand (TOA) were decreased after adsorption steps of the shortlength ligand (DETA) from 0.25 to 0.5 layers and from 1.25 to 1.5 layers. It is possibly attributed to substitutions of TOA with bulky hydrocarbon chains to DETA with a shorter hydrocarbon length. It is noted that when the Pt NP layer was deposited, it is difficult to notify changes in the FT-IR spectra possibly due to small amounts of the Pt NP adsorption. This is further confirmed with X-ray photoelectron spectroscopy (XPS) measurements, described in a later section.

To evaluate the catalytic HER activity, linear sweep voltammetry (LSV) analysis was performed under an acidic condition of 0.5 M H_2SO_4 (Figure 2f,g). Samples of Pt sputtered onto the Ti substrates were also tested for comparison with the AuPtn LbL films. The average overpotentials at a current density of 10 mA cm⁻² were obtained from three measurements. A comparison of the activity of more AuPtn samples in acidic conditions is shown in Figure S5. As the number of repeated depositions increased, the overpotentials gradually decreased and reached ~100 mV for the AuPt10 sample. It is attributed to the increase in the absolute amounts of the Pt loading. The AuPt10 LbL sample with a thickness of ~60 nm contained a small Pt loading, i.e., 1.5 μ g cm⁻², which is only 0.73 wt % of the total mass (obtained by inductively coupled plasma mass spectrometry (ICP-MS) analysis and quartz crystal microbalance (QCM). (See Table S1 and Experimental Section for details.) Notably, for the AuPt15 LbL sample with an estimated thickness of ~90 nm, the overpotentials decreased to 66 mV. In comparison, the LSV of only Ti substrate and Pt sputtered on Ti substrate were additionally measured in acidic and alkaline media. The Pt sputtered on a Ti substrate sample showed an overpotential of

62 mV with a similar thickness. Only the Ti substrate sample did not show meaningful HER activity.

To examine the structures of the Au-Pt LbL samples, transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX) were performed (Figures 3 and S6). The TEM specimens were prepared by depositing nanoparticles using LbL assembly on a carbon-coated Cu grids as a substrate. The EDX mapping images (Figures 3b-d and S6) show the distributions of the Au and Pt atoms. Most of the bright regions corresponding to Au overlapped with the spots for Pt, indicating mixed and random distributions of Au and Pt NPs in the LbL nanocomposite films. The size and intensity of bright spots for Pt atoms were smaller than those for Au atoms, attributable to the mass ratio (99.27:0.73) of Au and Pt atoms in the AuPt10 sample (Table S1). In highresolution TEM images (Figure 3e,f), randomly oriented lattice fringes with d-spacing values of 0.226 and 0.237 nm were observed, corresponding to the (111) planes of Pt and Au, respectively. The selected area electron diffraction (SAED) pattern of AuPt10 (Figure 3g) exhibited spotted ring patterns typical of polycrystalline structures, indicating random orientations of Au and Pt NPs in the composite films. Also the AuPt3 samples with less deposition numbers were examined by TEM (Figures S6). Similar to the AuPt10 samples, randomly oriented lattice fringes were observed with a *d*-spacing of 0.237 and 0.226 nm, corresponding to the (111) planes of Au and Pt, respectively (Figure S6c). EDX maps also showed major distribution of Au element and minor appearance of Pt element. It is noted that the sizes of NP agglomerates bigger in the AuPt10 sample were than those in the AuPt3 sample. Organic phases were difficult to discern in the TEM analysis, potentially owing to the low contents and



Figure 4. FE-SEM images of (a) Au20, (b) Pt20, and (c) AuPt10 samples. (d) LSV polarization curves and (e) Tafel plots of Au20, Pt20, and AuPt10 samples, Pt sputtered onto Ti and Ti substrate in 0.5 M H_2SO_4 . (f) Electrochemical impedance spectroscopy (EIS) of Au20, Pt20 and AuPt10 samples at -0.3 V vs RHE (inset: enlarged Nyquist plots of the two electrodes and equivalent circuit used for data analyses).



Figure 5. XPS spectra of (a) Au 4f, (b) Pt 4f, and (c) N 1s peaks in Au20, Pt20, AuPt10, TOA-AuNP, and TOA-PtNP; and Pt 4f peaks in (d) TOA-PtNP, (e) Pt20, and (f) AuPt10 samples.

metallic fusion between Au and Pt crystals.²⁸ Additionally, the crystal structures of the Au–Pt LbL samples were characterized by X-ray diffraction (XRD) (Figure S7). The XRD pattern of AuPt10 sample showed small peaks, marked with yellow circles in Figure S7a, at angles of 38.2, 44.4 and 64.6° that are associated with the (111), (200) and (220) facets of Au crystallites, respectively. However, Pt peaks were difficult to

identify for both samples due to small amounts of Pt loadings and strong Ti peaks.

To evaluate the enhancement of the HER activities of AuPt nanocomposite films, control samples of Au20 and Pt20 were fabricated (Figure 4). The AuPt10 sample with the same total number of NP layers was selected as a representative case among the Au-Pt LbL films. The FE-SEM image of the Au20

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sample showed that its morphology was more uniform than that of the AuPt10 sample. The Pt20 sample exhibited an irregular surface morphology, likely because of the small size of Pt NPs with lower coordination numbers for the attached NPs. The UV-vis absorbance spectra (Figure S8) indicated that the absorbance intensities of Au and Pt LbL samples gradually increased, whereas the Pt samples exhibited low intensities for the same number of depositions of NP layers. This result was consistent with the FE-SEM results for the Pt samples. It was difficult to form homogeneous films with the only-Pt/DETA LbL configuration; however, uniform AuPt LbL films could be obtained by alternately depositing DETA/AuNP layers, as shown in Figures 2 and 4c. The AuPt10 sample exhibited a higher catalytic activity and lower overpotential and Tafel slope than the Au20 and Pt20 samples (Figure 4d,e). Furthermore, the overpotential of the AuPt10 sample was two times lower than that of the Pt20 sample, despite the Pt content being 25% lower than that of the counterpart with the same area. When comparing the HER activity of AuPt10 electrode to other previous studies, AuPt10 shows higher or similar activity than other electrocatalysts with similar levels of Pt loadings (Table S2). Electrochemical impedance spectroscopy (EIS) was analyzed over a frequency range of 100 kHz to 0.1 Hz in 0.5 $M H_2SO_4$ (Figures 4f and S9). Experimental results were fitted by a simplified equivalent circuit model (inset in Figure 4f), where R_s represents the solution resistance, and R_{ct} and C_{dl} represent charge transfer resistance and double layer capacitance at interface, respectively. AuPt10 exhibited a significantly lower R_{ct} value of 6.4 Ω than that of Pt20 and Au20 with R_{ct} values of 739.4 and 852.9 Ω , respectively, whereas R_s is almost consistent for the three electrocatalysts. Nonuniform depositions of Pt NPs for Pt20 samples also could effect on the low level of charge-transfer observed in EIS data. It indicates that facile electron transfer on AuPt10 mainly leads to increase HER compared to Pt20 and Au20. Also various potentials from -0.05 to -0.4 V were applied to obtain the corresponding Nyquist plots for the AuPt10 sample (Figure S9). R_{ct} significantly decreased from 14.7 Ω at -0.05 V to 4.4 Ω at –0.4 V, indicating enhanced electron transfer kinetics in HER with increasing overpotentials.^{36,37} In addition, the electrocatalyst activity in alkaline electrolytes was evaluated (Figure S10). Compared to acidic conditions, it has 2-3 times higher overpotential in alkaline conditions, and in general, the HER activity of platinum-based catalysts showed similar trends.³⁸⁻⁴⁰ A comparison of the activity of more AuPtn samples in alkaline conditions is shown in Figure S11. As in the case of acidic electrolytes, the activity increased with the number of layers, and the Au-Pt LbL films outperformed the other control samples with only Pt and Au LbL films.

X-ray photoelectron spectroscopy (XPS) analysis was performed to investigate the electronic states of the samples (Figure 5). In addition to the Au20, Pt20, and AuPt10 samples, Au and Pt NPs with TOA as the stabilizing agent from the pristine NP dispersions were examined. No notable peak changes were observed in O 1s and Ti 2p for Au20 and AuPt10 samples (Figure S12). In the case of the Pt20 sample, intense peaks were observed in the O 1s and Ti 2p due to irregular depositions of Pt NPs with exposure of the surface of the titanium oxide substrate. In the N 1s spectra of the pristine NP samples, two peaks were observed near 398.9 and 401.8 eV for TOA-Au and TOA-Pt, attributed to N–C and N⁺, respectively. In contrast, Au20, Pt20, and AuPt10 samples exhibited a single N 1s peak near 399.2 eV, attributed to N–C. The disappearance of quaternary amine peaks in the NP LbL films indicated that successful ligand-exchange processes occurred between TOA and DETA during LbL assembly. In the Au 4f spectra of Au20, two main peaks at 83.48 and 87.08 eV were observed, attributed to $Au^0 4f_{7/2}$ and $4f_{5/2}$, respectively. The peaks for the AuPt10 sample exhibited no shift (<0.1 eV) compared to the Au20 sample (Figure S13). This means that there is no significant chemical interaction between the deposited Au particles and the other particles. To clarify the changes in the Pt 4f peaks, Pt $4f_{7/2}$ and $4f_{5/2}$ were deconvoluted into two oxidation states of Pt^0 and Pt^{2+} . Detailed information about the deconvolutions is in Table S3. Compared to the TOA-Pt NPs, the Pt 4f peaks of the Pt20 and AuPt10 samples exhibited negative shifts with magnitudes less than 0.9 eV, possibly due to ligand exchange. In general, the TOA-Pt NPs are expected to exhibit a strong proton adsorption inactivity for HER, because they contain under-coordinated sites.⁴¹ The binding strength for the LbLassembled Pt20 and AuPt10 films was lowered. The positive shift of the Pt 4f peaks for the AuPt10 sample in comparison to that of the Pt20 sample can be attributed to the downshift of the *d*-band center of Pt,⁴² which can promote the hydrogen adsorption for Pt $(Pt-H_{ad})$ and accelerate the recombination of H_{ad} with H₂.⁴³

In addition to the electronic effects, high electrical conductivities and electrochemically active surface areas (ECSAs) likely contributed to the high activities of the Au-Pt LbL films. Highly conductive supports for the Pt electrocatalysts have been introduced to facilitate fast charge transfer^{3,44} and electron transport for HER kinetics.^{45,46} The electrical conductivity of the Au-Pt LbL films was measured to be 8.7×10^4 S cm⁻¹, which was similar to that of bulk Pt (9.4 \times 10⁴ S cm⁻¹)⁴⁷ owing to the ligand exchange-assisted LbL assembly. Additionally, it was confirmed that the AuPt10 LbL sample exhibited metallic conduction behavior (Figure \$14).^{28,48} Electrical resistances were obtained in the temperature range from 2 to 300 K, that was fitted with first order linear equation $((R_{(T)}-R_{(2)})/R_{(2)} = \alpha \Delta T$, where $R_{(T)}$ and $R_{(2)}$ are resistances at temperatures T and 2 K, respectively). This showed linear increase of resistances along the absolute temperature with a positive slope of $\alpha = 9.34 \times 10^{-4}$, indicating the metallic conduction behavior of the AuPt sample.⁴⁹ Furthermore, ECSA of Au-Pt LbL film was determined using the charge associated with a hydrogen adsorption or desorption obtained in a cyclic voltammetry. The Au–Pt LbL films exhibited a high ECSA of 306 $\text{cm}^2 \text{ g}^{-1}$ (Figure S15), which is more than three times higher than that of the Pt20 samples (83 cm² g⁻¹). Stability of the Au–Pt LbL films was examined with cyclic voltammetry and chronoamperometry (Figure S16). The AuPt10 electrode showed stable electrocatalytic activity up to 500 cycles, but the HER activity decreased at 2000 cycles (Figure S16a). The FE-SEM image of the AuPt10 electrode after 2000 cycles showed aggregations and partial losses of the nanoparticles on the surface in Figure S17a,b. The XPS spectra showed reduction of Pt^{2+} and N-Cpeaks for the samples after 2000 cycles (Figure S17c-e), also indicating coalescence and disintegration of the nano-particles. 52,53 Such deterioration can be attributed to degradation of stability with partial dissolution for Au and Pt under acidic condition with prolonged electrochemical tests.⁵⁴⁻⁵⁷ In the chronoamperometry test at -0.1 V, initial current density of the AuPt10 electrode was corresponded well to the value measured at LSV. However, the current densities

got gradually decreased due to the deterioration and physical loss, accompanied by H_2 bubble detachment, of catalysts.^{58–60}

3. CONCLUSIONS

We fabricated Au-Pt bimetallic nanocomposite electrocatalysts for HER via ligand exchange-assisted LbL selfassembly. Through ligand exchange, bulky TOA-Br ligands on the surface of Au and Pt NPs were replaced with DETA, a short alkyl amine, to form uniform films with a metal-level conductivity (8.7 \times 10⁴ S cm⁻¹). With an increase in the number of depositions, the overpotentials gradually decreased with the increase in the Pt loading. The AuPt15 LbL nanocomposites films exhibited an overpotential of 66 mV at 10 mA cm⁻² with a significant small Pt loading of 0.73 wt %. This result suggested that the HER activity was significantly enhanced, attributed to the synergistic effect of the uniform depositions of bimetallic heterostructures, rapid charge transfer owing to increased electrical conductivity, and increased electrochemical surface area owing to the nanotexture of the LbL-assembled films. Therefore, ligand-exchange-assisted LbL self-assembly represents a facile and versatile method for largearea production of multicomponent electrocatalysts from wetsynthesized NPs.

4. EXPERIMENTAL SECTION

Synthesis of Au and Pt Nanoparticles. To synthesize the spherical Au NPs, 30 mL of an aqueous solution of 30 mM gold(III) chloride trihydrate (HAuCl₄· $3H_2O$) was added to 25 mM TOABr in 80 mL of toluene solution with continuous stirring. Subsequently, 25 mL of a 0.4 M aqueous solution of sodium borohydride (NaBH₄) was slowly added as a reducing agent, and the mixture was stirred for 3 h to form gold(0) NPs. The mixture was stabilized to separate the organic phase and washed with 0.1 M H₂SO₄, 0.1 M NaOH, and deionized water thrice. The same process was used to synthesize Pt NPs, except that the Pt precursor chloroplatinic acid hydrate (H₂PtCl₆· xH_2O) was used instead of the gold precursor.

Fabrication of LbL-Assembled Nanocomposite Electrocatalyst Films. A Ti substrate was treated with 400 grit sandpaper and then washed with acetone. Quartz or slide glass substrates were cleaned through RCA treatment (H_2O : NH_4OH : H_2O_2 in a 5:1:1 volume ratio) at 70 °C. The silicon substrate was cleaned with a piranha solution (H₂SO₄: H₂O₂ in a 7:3 volume ratio). For the ligandassisted LbL assembly, prelayers of PEI (Mw \approx 50,000-100,000) were deposited onto the cleaned substrates by dipping in 5 mg mL $^{-1}$ aqueous solution for 30 min and washing with deionized water. The PEI-coated substrate was dipped into Au or Pt NP dispersions in toluene for 30 min. Subsequently, the substrate was washed with pure toluene to remove the weakly adsorbed NPs. Next, the substrate was dipped in a DETA solution (10 mg mL⁻¹) in ethanol for 20 min and washed with pure ethanol for the ligand-exchange step. Subsequently, the previous deposition processes of NPs and DETA were repeated to achieve the target number of depositions.

Characterization. Fourier transform infrared (FTIR) spectra were analyzed with a Nicolet iS50 (Thermo Fisher Scientific) instrument operating in the attenuated total reflection (ATR) mode. The surface morphologies were analyzed by FE-SEM (Apreo S Hivac, S-4800) at an acceleration voltage of 15 kV. UV–vis spectra were obtained to investigate the deposition behavior of nanocomposite films using a Lambda 365 instrument (PerkinElmer). TEM images and energy dispersive X-ray spectroscopy (EDX) data were obtained with a JEM 2100F instrument at an acceleration voltage of 200 kV. Before the observations, the samples were directly fabricated using carbon-coated Cu grids (200 mesh) as substrates. X-ray diffraction (XRD) was employed for phase analysis and structural characterization (D8 ADVANCE, BRUKER). The metal contents of the LbL multilayered films were determined by using an ICP-MS (Agilent 7700X ICP-MS) instrument. XPS analysis was performed using a

NEXSA device (ThermoFisher Scientific) with an Al-K α X-ray source. The binding energies (eV) were obtained by shifting the C 1s spectra to 284.8 eV. To determine the conductivity of the synthesized sample, the sheet resistance was measured using a four-point probe (CMT-SR1000N, Advanced Instrument Technology). The temperature-dependent electrical resistance was measured by a physical property measurement system (PPMS-9, Quantum Design). Electrochemical measurements were performed in a standard three-electrode cell with a Zive SP1 device (ZIVELAB). The reference electrode was a Ag/AgCl electrode in 0.5 M H₂SO₄ and 1 M KOH electrolytes, and Pt sputtered on FTO was used as the counter electrode. To perform the HER experiments, we obtained cathodic LSV scans at a scan rate of 50 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) analysis was carried out from 100 kHz to 0.1 Hz in 0.5 M H₂SO₄. To confirm the stability and determine the ECSA, CV analysis was performed in a $0.5 \text{ M H}_2\text{SO}_4$ solution at a scan rate of 0.5 V s^{-1} . Chronoamperometry was measured at an applied potential of -0.1 V vs RHE. All potentials were converted to the corresponding potentials versus RHE. The Pt loading in AuPt15 was estimated from the measured mass of the AuPt sample over the QCM electrode. The mass ratio of Au:Pt determined from ICP-MS was used to determine the Au and Pt contents.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.3c01739.

ICP-MS analysis for loading amount of Au20, Pt20, and AuPt10 samples; comparison of the HER activity in acidic electrolyte of Au–Pt catalyst with low amount Ptbased catalysts reported in literature; deconvolution of XPS spectra; characteristic of Au and Pt NPs; characteristic of AuPtn samples; polarization curves of AuPtn and Au20, Pt20, AuPt10, and Pt on Ti, Ti foil electrodes; EIS of AuPt10 at various overpotentials in acidic electrolyte; XPS spectra of C 1s, O 1s, Ti 2p, and Au 4f peaks; resistance ($R_{(T)}/R_{(2)}$) vs temperature (K) of AuPt10 sample; CV curves for ECSA of the AuPt10 electrode; stability tests of AuPt10 electrode; FE-SEM images and XPS spectra of before and after 2000 cycles of AuPt10; LSV polarization curves for AuPt10 sample at different counter electrodes (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Youn Jeong Jang Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea; orcid.org/0000-0002-2400-0473; Email: yjang53@ hanyang.ac.kr
- Bongjun Yeom Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea; orcid.org/0000-0001-8914-0947; Email: byeom@ hanyang.ac.kr

Authors

- Sujin Lee Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea; orcid.org/ 0009-0003-4414-2959
- Yongkwon Song Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, United States; Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Republic of Korea; © orcid.org/0000-0002-2173-8157
- Jinhan Cho Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Republic of Korea; ⊚ orcid.org/0000-0002-7097-5968

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.3c01739

Notes

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