Network of Heterogeneous Catalyst Arrays on the Nitrogen-Doped Graphene for Synergistic Solar Energy Harvesting of Hydrogen from Water

Sang Rim Shin,‡ Jung Hyo Park,† Keon-Han Kim,† Kyung Min Choi,*§ and Jeung Ku Kang*†‡

†Department of Materials Science and Engineering and ‡Graduate School of Energy, Environment, Water, and Sustainability (EEWS), Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea
§Department of Chemical and Biological Engineering, Sookmyung Women’s University, 100 Cheongpa-ro 47 gil, Yongsan-gu, Seoul 140-742, Republic of Korea

ABSTRACT: Combination of different nanoparticles has been suggested as a promising approach to realize advanced functionalities for many applications. Herein, we report a new method to make uniform sized nanoparticle arrays in a network by arranging a micelle monolayer in an ordered fashion on the conductive nitrogen-doped graphene (NG). Moreover, coarrangement of two different arrays using both metal and metal oxide nanoparticles on the conductive graphene is found to result in the synergistic and cooperative photocatalytic activity for production of hydrogen from water using solar energy, with the excellent performance attributed to efficient electron transfer from one nanoparticle through the conductive NG to the other nanoparticle in a single-layer network. Consequently, this work suggests a promising solution to design high-performance catalysts in a network of different nanoparticle arrays on thin and flexible conductive substrates.

INTRODUCTION

Nanomaterials have been widely studied for their unique functions and have been combined with other materials in many applications.1−4 The combination of different nanomaterials for controlled functionalities has been usually done by simply mixing different functional nanomaterials or attaching one on the surface of another material to make them work cooperatively.5−9 However, it is still challenging for one to realize a size-controlled nanoparticle network on a thin and flexible conductive substrate such as graphene.10,11 For example, the small nanoparticles with increased surface energy tend to aggregate; thus, it is very hard to arrange the size-controlled morphology on a thin and flexible conductive layer.12−16 Another challenge was also identified to be associated with the lack of arrangements of different nanoparticles in a network where nanoparticle arrays could provide synergistic and cooperative functionalities, akin to an interconnected system such as the electronic circuit. Also, hydrogen, which can be reproduced by photocatalytic splitting of pure water using solar energy,17,18 contains much larger chemical energy per mass 142 kJ g−1 than any hydrocarbon fuel. In this view, only about 4 kg of hydrogen, which is burned electrochemically with oxygen from air in a hydrogen fuel cell, is required to cover the range of about 300 miles of a gasoline-powered car while generating only environmentally clean water as a byproduct. Consequently, hydrogen is considered to be an ideal fuel for solving an energy crisis and alleviating the earth’s environmental problems resulting from the use of petroleum fuels.

Here, we report a new method to arrange different functional nanoparticles with uniform sizes and interparticle distances on the nitrogen-doped graphene (NG) constructing network (Figure 1). Especially, the fabricated ordered arrays of TiO2, Cu, Fe, and Pt nanocrystals with controlled sizes on an NG layer were demonstrated using a micelle monolayer, where the micelle has a good affinity towards the precursors for formation of nanoparticles, and the graphene plays as a channel for efficient transfer of solar energy-driven electrons.

Moreover, the Pt and TiO2 nanoparticle arrays with graphene in the single-layer network were prepared to explore the synergistic effect for solar energy harvesting of hydrogen from water. It is notable that the hydrogen production rate on this catalyst network is higher by about 19-fold than that on a silicon substrate, thus implying that the network enabling efficient electron transfer between two functional nanoparticles

Received: July 7, 2016
Revised: October 7, 2016
Published: October 10, 2016

DOI: 10.1021/acs.chemmater.6b02780
Chem. Mater. 2016, 28, 7725−7730
is very important for the design of high-performance photocatalysts.

**EXPERIMENTAL SECTION**

**Graphene Film Synthesis.** All chemicals and solvents were used without further purification. At first, graphene oxides (GOs) were synthesized from natural graphite by the modified Hummers’ method.19,20 The 2 g sample of the powdered flake graphite (Aldrich, ≥99.99%, Lot MKBNS5560V) was dipped in an acid solution where 1 g of NaNO₃ (Sigma-Aldrich, ≥99.9%, Lot MKBV7820V) was dissolved in 46 mL of H₂SO₄ (Junsei, GR, 95%, ≥98%, 83010-1250; caution: the sulfuric acid is a highly corrosive strong mineral acid). The ingredients were mixed in the round bottom flask with stirring and were cooled to 0 °C in an ice bath. After cooling down, 6.3 g of KMnO₄ (Sigma-Aldrich, ≥99.99%, Lot MKBS9418V; caution: potassium permanganate is hazardous in case of skin contact) was added very slowly with vigorous agitation keeping the temperature below 20 °C. Then, the ice bath was removed, and the flask was maintained at 55 ± 3 °C for 2 h. The mixture became pasty with evolution of a small amount of gas. After 2 h, 92 mL of water (Duksan, HPLC grade) was slowly stirred into the paste, causing violent bubbling and an increase in temperature to 98 °C. The diluted suspension, brown in color, was maintained at this temperature for 1 h. The suspension was then further diluted with 100 mL of warm water and 30 mL of 30 wt % of hydrogen peroxide solution (Junsei, GR, 99.0%, 6726) to reduce the graphene oxide, the fully oxidized graphite (Aldrich, ≥99.5%, 634662, Lot MKBJ0873V) was physically mixed with 1 g of isopropoxide (TTIP) (Aldrich, 97%, Lot SHBD7778V) on the P4VP copolymer, polystyrene−block-poly(4-vinylpyridine) (PS−b-P4VP) (Sample P110-S4VP, 47600−20900, M₉/M₈, 1:1.4, Polymer Source Inc.), in toluene (Sigma-Aldrich, Chromasolv plus for HPLC ≥ 99.9%). After being annealed at 75 °C for 3 h with stirring, the solution was spin-coated on the NG film at 2000 rpm for 60 s. The spin-coated substrate was immersed in pure methanol (Sigma-Aldrich, Chromasolv, for HPLC, ≥99.9%, Lot SHBC9819V) at room temperature for 10 h. During that time, the PS composing the upper part of the micelle was easily dissolved in methanol, and finally the core part of the micelle, the P4VP region, was exposed. Then, we deposited titanium(IV) isopropoxide (TTIP) (Aldrich, 97%, Lot SHBD7778V) on the P4VP core sites with vaporized water in order to form TiO₂ nanoparticles. In this process, we prepared a sealed container (1.2 L size) containing 5 mL of DI water (stored in a 20 mL vial), and the micelle coated NG film was heated in a 60 °C convection oven for 5 h. Then, after the DI water vial was replaced with another vial (20 mL) containing 3 mL of TTIP, the container was kept at 60 °C for another 8 h. Next, the substrate was rinsed by dipping in ethanol (Duksan, HPLC grade) several times, and then the micelle template was removed through heat treatment under nitrogen flow (100 sccm) at 400 °C for 30 min.

**Cu-on-NG, Fe-on-NG, and Pt-on-NG Synthesis.** Each nanoparticle array was fabricated using a micelle with the precursor. The micelle solution was prepared by dissolving 0.5 wt % of diblock copolymer, polystyrene-block-poly(4-vinylpyridine) (PS−b-P4VP) (Sample P110-S4VP, 47600−20900, M₉/M₈, 1:1.4, Polymer Source Inc.), in toluene (Sigma-Aldrich, Chromasolv plus for HPLC ≥ 99.9%). After the solution was annealed at 75 °C for 3 h with stirring, CuCl₂·H₂O (Sigma-Aldrich, ReagentPlus, purified, ≥ 99%, 224332), FeCl₃ (Sigma-Aldrich, Reagent grade, 97%, 157740, Lot MKBF3037V), or H₂PtCl₆·H₂O (Sigma-Aldrich, 99.995%, 254029), precursors of Cu, Fe, and Pt nanoparticles, respectively, was added to the micelle solution. The molar ratio of precursor the P4VP units was fixed at 0.5 for all of the samples. Then, the solution was stirred for 3 days at ambient temperature and filtered with the 0.2 μm syringe filter (Advantec, PTFE, hydrophilic). The micelle solution containing metal precursor was spin-coated on the NG film at 2000 rpm for 60 s. The substrate was rinsed with ethanol (Duksan, HPLC grade) several times, and the micelle template was removed by heat treatment under nitrogen flow (100 sccm) at 400 °C for 30 min (overall coating procedure is the same as the one for TiO₂-on-NG synthesis).

**TiO₂/Pt/Pd Powder Preparation.** All chemicals and solvents were used without further purification. A 1 g sample of TiO₂ (Sigma-Aldrich, 99.5%, 634662, Lot MKBJ0873V) was physically mixed with 1 wt % of commercial platinum nanoparticles (Sigma-Aldrich, 99.9%, 771937, Lot MKBTP9751V) and synthesized NG powders using the mortar.

**Materials Characterization.** SEM (JSM-7600F, JEOL) and TEM (JEEM-ARM200F, JEOL) were used to analyze the microstructure of a sample. The atomic bonding configurations of the NG surface were obtained through the XPS (Kratos Thermo VG Scientific) analysis. The Raman spectroscopy (excitation, 514 nm, high-resolution Micro Raman/low temp, PL System, LabRAM HR UV–vis–NIR PL) measurement was also used to investigate the characteristics of graphene materials. The TXRF (total X-ray reflection fluorescence spectrometer, Nano hunter, Rigaku Corporation, Mo source) elemental analysis was carried out to confirm the components of the structure. In order to derive the average lifetime of a charge carrier, the time-correlated single photon counting (TCSPEC, Edinburgh EPLED-300) fluorescence lifetime measurement with EPLs (picosecond pulsed diode lasers) has also been performed. Full characterization details are provided in the Supporting Information (SI).

Figure 1. Schematic illustration of heterogeneous catalyst arrays on the NG in a single-layer network.
Photocatalytic Performance Test. The sample was put in the cylindrical quartz reactor with the small magnetic stir bar and 80 mL of water solution with 25 vol % of methanol. The reactor was closed with a rubber septum and completely sealed with hot melt adhesive. Then, the inside of the reactor was purged with argon (99.999%) for 30 min. The photocatalytic reaction was started on irradiation of photons using a 300 W xenon lamp (Newport, ozone free xenon arc lamp, 6258) with mild stirring. The light source was equipped with a cooling system and an IR cutting filter, and the average light intensity was determined to be 150 mW/cm² on the sample surface. The 100 μm of vapor inside the chamber was collected using a gas tight syringe with a volume reproducible adapter, and the syringe was purged with argon several times before capturing the vapor. The captured reactant was analyzed by the gas chromatograph (7890A, Agilent Technologies) with a thermal conductivity detector (TCD). This gas analysis instrument consisted of the packed column and 5 Å molecular sieves along with the carrier gas argon. According to a retention time, each component of the product gas was identified, and its concentration was determined by integrating each peak area. The final amount of hydrogen produced from water was calculated by calibration curves derived from the standard mixture gas. The quantum yield (QY) has been also determined. Details for calculation of the photocatalytic efficiency have been provided in the Supporting Information (S1).

RESULTS AND DISCUSSION

The aqueous graphene oxide was synthesized, and it was spin-coated on Si substrate with a native silicon oxide layer in the first step. Then, nitrogen was introduced onto the graphene oxide by means of the plasma-enhanced chemical vapor deposition (PECVD) process to make an NG film, which was annealed at 300 °C for 3 h under a H₂ atmosphere to remove the residual functional groups from the surface. The resulting film (Figure S1) was shown to have some wrinkles, and its atomic bonding configurations (Figure S2) through the X-ray photoelectron spectroscopy (XPS) analysis demonstrate that the amount of C–O bonding has been significantly reduced while that of C–N bonding is increased compared to that of the graphene oxide. This confirms the formation of the increased sp² nitrogen configurations in an NG film. Moreover, the Raman spectra of Figure S3 support an increased defect ratio by nitrogen doping in the NG film, and Table S1 shows the chemical compositions on the surfaces of NG and graphene oxide. The results signal that its abundant sp² nitrogen of the NG film could give a good affinity toward micelles and metal precursors while resulting in good conductivity to give efficient transfer of solar-driven electrons from one functional nanoparticle to another functional nanoparticle.

The arrays of TiO₂, Cu, Fe, and Pt nanoparticles on the NG, which are hereafter referred to as TiO₂-, Cu-, Fe-, and Pt-on-NG, respectively, have been prepared with the following procedures. The method to synthesize each nanoparticle array depends on the phase of a precursor. For Cu, Fe, and Pt on the solid precursors, each micelle solution was prepared by dissolving 0.5 wt % of PS-b-P4VP (47.6k–20.9k) in toluene which was then followed by mixing with the metal precursor. After 3 days of stirring, the solution was filtered with a syringe filter (0.2 μm) and then spin-coated onto the NG/Si substrate. The results show that these processes lead to a metal-loaded micelle monolayer on the NG. Meanwhile, for TiO₂ on a liquid precursor, a micelle solution without the precursor was spin-coated onto the NG (Figure S4) and then submerged in a pure methanol solution for 10 h to expose the core part of the micelle (P4VP). This was then placed in a chamber containing the titanium(IV) isopropoxide (TTIP) vapor for 8 h as described in our previous study. Next, the micelle template was removed through heat treatment at 400 °C for 30 min. The resulting nanoparticle arrays on the NG were verified by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), while the chemical composition was determined by the total X-ray fluorescence (TXRF) analysis. Meanwhile, for fabrication of the two different nanoparticle arrays, each nanoparticle was deposited consecutively onto the graphene by repeating each process described above. In particular, a single-layer networked array of Pt and TiO₂ nanoparticles on the graphene was investigated using TEM, STEM, TXRF, and XPS analyses. Also, its photocatalytic performance was explored as an exemplar case to demonstrate the synergistic reaction in a single-layer network. Furthermore, the TCSPC measurements were made to investigate the electron migration from one functional nanoparticle to another functional nanoparticle.

The ordered arrays of TiO₂, Cu, Fe, and Pt nanoparticles with uniform sizes and interparticle distances are found to be arranged in an ordered fashion onto the NG. The SEM images (Figure 2a,d,g,i) showed that the nanoparticles are on ordered arrays, which demonstrate the advantageous property compared to other graphene composites that could be typically aggregated. Moreover, the wrinkles of NG have been observed on SEM images. These show that the micelle monolayer operates as a template layer for the well-arranged formation of nanoparticle arrays on the NG by preventing agglomeration during the nanoparticle synthesis process. In addition, Figures S5 and S6 demonstrate that the average particle sizes of TiO₂, Cu, Fe, and Pt are about 23.9, 25.6, 25.3, and 26.8 nm while their standard deviations are 2.22, 2.28, 2.97, and 2.19 nm, respectively. The morphology and lattice

Figure 2. Structural and compositional analyses of TiO₂-on-NG, Cu-on-NG, Fe-on-NG, and Pt-on-NG, where their corresponding SEM images are shown in parts a, d, g, and j. Also, the TEM images are shown in b, e, h, and k with the HRTEM images in their insets while the elemental analysis spectra are presented in c, f, i, and l.
structure (Figure 2b,e,h,k) of each nanoparticle arranged on the NG were also examined using the TEM. To prepare the TEM specimens, the nanoparticle-on-NG was covered by a poly-(methyl methacrylate) (PMMA) layer, after which a silicon oxide layer was etched out by submerging the sample in a 0.1 M sodium hydroxide (NaOH) solution. The desired film with the PMMA supporting layer was then transferred to the TEM grid while the remaining polymer layer was removed by heating. The TEM image in Figure 2b shows the TiO2 nanoparticle array on the NG, and the high-resolution TEM (HRTEM) image in its inset supports that the d-spacing of the lattice fringe is approximately 0.34 nm corresponding to the anatase (101) phase. Figure 2c,f,i,l also shows the Cu, Fe, and Pt nanoparticle arrays where the d-spacings in their insets at 0.203, 0.199, and 0.226 nm correspond to those for Cu(111), Fe(110), and Pt(111), respectively. The elemental composition spectra for each nanoparticle in Figure 2c,f,i,l were also obtained through the TXRF analysis.

The Pt and TiO2 nanoparticles are also selected and coarranged on the NG, and the synergistic effect of this single-layer network on a photocatalytic hydrogen production from water has been determined. The synthesis process is described in Figure 3a. At first, the micelle loaded with the Pt precursor was deposited onto the NG by spin-coating to give Pt-on-NG. After removal of the sacrificial micelle template, another micelle monolayer without a precursor was spin-coated onto the surface of the Pt-on-NG. The subsequent procedures in each step are identical to those used during the creation of the single nanoparticle array on the NG. These consecutive methods result in a single-layer networked array of Pt and TiO2 nanoparticles together on the NG, referred to as the (Pt + TiO2)-on-NG. Next, the structure and composition of this sample were examined by SEM, TEM, STEM, TXRF, and XPS analyses. Figures S7 and S8 show SEM and TEM images of the (Pt + TiO2)-on-NG, where Pt and TiO2 nanoparticles were found to be well-arranged on the NG. STEM images (Figure 3b,c), which can distinguish different atomic numbers according to the contrast, indicate that the brighter particles in a high-angle annular dark field (HAADF) image (Figure 3c) are platinum nanoparticles and that the darker particles are TiO2 nanoparticles. Most of the TiO2 and Pt nanoparticles are shown to be attached separately on NG as shown in Figure 3b,c. Also, it is notable that a minority of Pt nanoparticles have been deposited with TiO2 nanoparticles. In addition, the TXRF elemental analysis (Figure 3d) proves the coexistence of two different Pt and Ti metal elements on the NG.

The C 1s spectra of Figure 4a show the peaks corresponding to C==C (283.52 eV), C—C (284.52 eV), C—N (285.59 eV), C−O (286.31 eV), C==O (287.07 eV), and O==C—O (288.01 eV) bonds. In addition, the N 1s spectra of Figure 4b represent that there are three different types of nitrogen configurations in the graphene including pyridinic N (N-6, 398.48 eV), pyrrolic N (N-5, 399.88 eV), and quaternary N (graphitic N, N-Q, 401.63 eV). In Pt 4f spectra of Figure 4c, there are two different configurations representing Pt0 (Pt 4f7/2 at 71.18 eV and Pt 4f5/2 at 74.27 eV) and PtII (Pt 4f7/2 at 72.46 eV and Pt 4f5/2 at 76.57 eV). Also, we found that the Ti 2p peak in Figure 4d consists of two subpeaks corresponding to Ti 2p1/2 (458.83 eV) and Ti 2p3/2 (461.5 eV). These results support that the (Pt + TiO2)-on-NG contains Pt and Ti, consistent with those obtained through the TXRF analysis of Figure 3d.

The photocatalytic performance for hydrogen production reaction in aqueous solution has also been tested. The photoreaction was demonstrated in a quartz reactor under irradiation by a xenon lamp with an IR-cutting filter while the reactor was completely sealed. The light source was equipped with a cooling system. The inside of the reactor was purged with argon for 30 min prior to the start of the photocatalytic reaction, and the amount of hydrogen was analyzed by gas chromatography with a thermal conductivity detector. The final amount of the produced hydrogen was calculated by the calibration curves derived from a standard mixture gas. In addition, we have investigated the effect of graphene in photocatalytic performance. Three different types of graphene materials including GO, reduced graphene oxide (RGO), and
NG were used as substrate. Figure S9 shows the photocatalytic hydrogen production rates for TiO$_2$-on-Si, TiO$_2$-on-GO, TiO$_2$-on-RGO, and TiO$_2$-on-NG. These demonstrate that the catalytic activity was varied according to the chemical composition of the graphene. The increase by about 2.8-fold in the hydrogen production rate of TiO$_2$-on-GO compared to that of TiO$_2$-on-Si is attributed to the fact that part of GO could be reduced to RGO under photoradiation, so that the part of TiO$_2$-on-GO can change into TiO$_2$-on-RGO sites efficiently for hydrogen production. After photoreaction for 24 h, we found that most of the C–O bonds composing the GO were broken, thus resulting in the significant decrease of the C–O peak intensity in the XPS C 1s spectrum. In contrast, the C 1s spectra of RGO and NG (Table S1) were found to be similar to the spectra obtained before photoreaction (Figure S10 and Table S2). These results are in good agreement with those of the previous study, showing that GO can be reduced when it is exposed to photocatalytic reaction with TiO$_2$.\textsuperscript{26}

Figure 5a demonstrates that the hydrogen generation rate of (Pt + TiO$_2$)-on-NG is much higher than that of TiO$_2$-on-NG, thus signaling that the electrons generated from TiO$_2$ nanoparticles transfer through the NG to the electron-accepting Pt nanoparticles. The hydrogen production rate is increased after 3 h, which is consistent in repeated measurements. We speculate that this increase originated from the activation procedure related to the surface tension of hydrogen bubbles in the aqueous solution, which is frequently observed in hydrogen production.\textsuperscript{24,27} In addition, Figure 5b shows that the average hydrogen generation rate of (Pt + TiO$_2$)-on-NG is approximately 19-fold higher than that of (Pt + TiO$_2$)-on-Si. In (Pt + TiO$_2$)-on-Si, it is notable that the photoexcited electrons from TiO$_2$ could not be transferred via the Si substrate, thus barely contributing to the photocatalytic reaction of the Pt nanoparticles. The recyclability of the (Pt + TiO$_2$)-on-NG has also been explored for 5 days along with each cycle having been performed for 24 h. Before starting each cycle, the atmosphere inside the quartz reactor was purged with argon for 30 min. The photocatalytic performance has also been determined through TCSPC measurements with the emission of a 520 nm laser to increase the temporal resolution of samples for picosecond fluorescence decays. The results of Figure 5d show that the average lifetime of the charge carriers in the (Pt + TiO$_2$)-on-NG (105 ps) is much shorter than that in (Pt + TiO$_2$)-on-Si (1.01 ns). In addition, the fluorescence decay spectra for TiO$_2$-on-Si, -GO, -RGO, and -NG are demonstrated in Figure S11, and the results show that the average lifetime with more conductive NG substrate is shorter than with less conductive substrates such as Si, Go, and RGO.\textsuperscript{28} Moreover, it is determined that TiO$_2$-on-NG has a hydrogen production rate that is about 1.5-fold higher than that of TiO$_2$-on-RGO. These observations support that the nitrogen-doped graphene has a better channel than the reduced graphene for efficient charge transfer resulting in production of hydrogen from water. These results support the contention that NG enables the rapid charge separation and transfer of photocreated electron–hole pairs before recombination.\textsuperscript{16,23}

In addition, the quantum yield of the (Pt + TiO$_2$)-on-NG for hydrogen generation was calculated to be 2.63% (see eqs S1–S3 and Figure S12), which is higher than the previous results.\textsuperscript{29} Moreover, the powder type sample has also been prepared by mixing of the NG, TiO$_2$ powder, and Pt nanoparticles, and we tested its photocatalytic activity, whose QY value of 0.35% is proven to be lower by about 7 times on (Pt + TiO$_2$)-on-NG. Also, the SEM image of Figure S13 shows that the morphology of (Pt + TiO$_2$)-on-NG was well-maintained after the photocatalytic performance test.

## CONCLUSIONS

In summary, we demonstrate a new method to arrange heterogeneous nanoparticles with controlled sizes and ordered arrangements on NG. First, we could fabricate the ordered array of each Cu, Fe, Pt, and TiO$_2$ nanoparticle on NG using a micelle template. Their structural and chemical compositions were examined by SEM, TEM, and TXRF. In addition, the two different Pt and TiO$_2$ nanoparticles were selected and coarranged as a specific monolayer arrangement on the NG to explore the networked synergistic effect for solar energy harvesting of hydrogen from water. It was found that the (Pt + TiO$_2$)-on-NG catalyst shows a higher activity by approximately 19-fold compared to that of the (Pt + TiO$_2$) on the silicon substrate. Furthermore, the TCSPC measurements demonstrated that the nitrogen-doped graphene facilitates separation of electron–hole pairs under light irradiation, in addition to having fast charge transfer, so that the NG operates to give the networked channel for efficient electron transfer between different functional nanoparticle arrays. Consequently, we expect that this work could pave a new route to design high-performance photocatalysts for many advanced applications including solar energy harvesting of hydrogen from water.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b02780.

Details of materials characterization, details for calculation of the quantum efficiency, and the experimental characterization data including SEM images, XPS, Raman spectra, TEM images, hydrogen production rates, Xe...
lamp spectra, TCSPC fluorescence decay data, Xe lamp spectra, and chemical compositions by XPS (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: kmchoi@sookmyung.ac.kr.
*E-mail: jeungku@kaist.ac.kr.

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Korea Center for Artificial Photosynthesis (2009-0093881), the Global Frontier R&D Program (2013M3A6B1078884) of the Center for Hybrid Interface Materials (HIM), and by the National Research Foundation of Korea (2016R1A2B3012053) funded by the Ministry of Science, ICT & Future Planning.

■ REFERENCES