

Photocatalysis

International Edition: DOI: 10.1002/anie.201601494
German Edition: DOI: 10.1002/ange.201601494A Conductive Hybridization Matrix of RuO₂ Two-Dimensional Nanosheets: A Hybrid-Type PhotocatalystJang Mee Lee⁺, Eun Kyung Mok⁺, Seul Lee, Nam-Suk Lee, Lamjed Debbichi, Hyungjun Kim,^{*} and Seong-Ju Hwang^{*}

Abstract: A universal methodology to efficiently improve the photocatalyst performance of semiconductors was developed by employing exfoliated RuO₂ two-dimensional nanosheets as a conducting hybridization matrix. The hybridization with a RuO₂ nanosheet is easily achieved by crystal growth or electrostatically derived anchoring of semiconductor nanocrystals on the RuO₂ nanosheet. An enhanced chemical interaction of inorganic semiconductor with hydrophilic RuO₂ nanosheet is fairly effective in optimizing their photocatalytic activity and photostability by the enhancement of charge separation and charge mobility. The RuO₂-containing nanohybrids show much better photocatalyst functionalities than do the graphene-containing ones. The present study clearly demonstrates that hydrophilic RuO₂ nanosheets are superior hybridization matrices, over the widely used hydrophobic graphene nanosheets, for exploring new efficient hybrid-type photocatalysts.

As an emerging member of low-dimensional nanostructures, exfoliated two-dimensional (2D) nanosheets (NSs) of layered metal oxide, are an area of intense research interest because of its extremely high morphological anisotropy and valuable functionalities.^[1,2] Among many metal oxide NSs, layered RuO₂ NSs show the highest electrical conductivity and sufficient chemical stability, which renders this material a useful building block for hybridization with a diversity of chemical species.^[3,4] Since the exfoliated NS, which is very thin, can create a strong electronic coupling with hybridized species,^[5] the hybridization with a metallic RuO₂ NS is expected to be effective in improving the photocatalytic activity of semiconducting inorganic solids through the enhancement of charge transfer (CT) and charge mobility. In fact, highly conductive graphene NSs have been widely

employed as an efficient hybridization matrix for enhancing the photocatalyst performance of diverse semiconductors, thus leading to a great deal of research activity on this topic.^[6] However, a strong self-stacking tendency of graphene NSs prevents homogeneous hybridization with photocatalyst crystals.^[7] Additionally the hydrophobic nature of graphene is not favorable for achieving strong chemical interactions with polar photocatalyst materials. The absence of such drawbacks for graphene renders the exfoliated RuO₂ NSs a better hybridization matrix than graphene for a diversity of semiconducting materials. However, at the stage of this submission, we were unaware of another report^[8] about the application of metallic RuO₂ NSs as a conducting hybridization matrix for exploring efficient hybrid photocatalysts.

In this work, exfoliated RuO₂ NSs are used as a conducting hybridization matrix for semiconductor nanocrystals of Ag₃PO₄ and CdS. The resulting RuO₂-based nanohybrids are tested as photocatalysts for the visible-light-induced generation of O₂ and H₂, and the photodegradation of organic molecules. Additionally the photocatalyst performance of the reduced graphene oxide (rG-O) based nanohybrids is also examined to estimate the relative efficiency of RuO₂ incorporation relative to the graphene addition. The dissimilar chemical interactions between RuO₂/rG-O and semiconductors are investigated with density functional theory (DFT) calculations and contact angle measurements.

The synthesis of monolayered RuO₂ NSs by the soft-chemical exfoliation process was evidenced by high-resolution transmission electron microscopy (HR-TEM), energy dispersive spectrometry (EDS), and atomic force microscopy (AFM) measurements (see Figure S1 in the Supporting Information). The RuO₂-Ag₃PO₄ nanohybrids were synthesized by the crystal growth of Ag₃PO₄ in the colloidal suspension of the exfoliated RuO₂ NSs (Figure 1A). The details of the synthetic conditions are provided in the Supporting Information. The obtained nanohybrids with the RuO₂/Ag₃PO₄ ratios of 0.025, 0.05, 0.075, and 0.1 wt % are denoted as RA025, RA05, RA075, and RA1, respectively. As plotted in Figure 1B, all the present RA nanohybrids exhibit typical X-ray diffraction (XRD) peaks of cubic silver orthophosphate phase (JCPDS no. 06-050), thus indicating the formation of Ag₃PO₄ crystals. No RuO₂-related Bragg reflections are observed, and strongly suggests a good dispersion of RuO₂ NSs. As demonstrated in the field emission-scanning electron microscopy (FE-SEM) images in Figure 1C, all the present RA nanohybrids show spherical Ag₃PO₄ particles anchored on the RuO₂ NS. The intimate coupling between RuO₂ and Ag₃PO₄ is confirmed by HR-TEM analysis which shows the lattice fringes of Ag₃PO₄

^[*] J. M. Lee,^[†] E. K. Mok,^[†] S. Lee, Prof. S.-J. Hwang

Department of Chemistry and Nanoscience
Ewha Womans University, Seoul 03760 (Korea)
E-mail: hwangsj@ewha.ac.kr

Dr. N.-S. Lee

National Institute for Nanomaterials Technology (NINT)
Pohang University of Science and Technology (POSTECH)
Pohang 37673 (Korea)

Dr. L. Debbichi, Prof. H. Kim

Graduate School of EEWS
Korea Advanced Institute of Science and Technology (KAIST)
Daejeon 34141 (Korea)
E-mail: linus16@kaist.ac.kr

^[†] These authors contributed equally to this work.

Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201601494>.

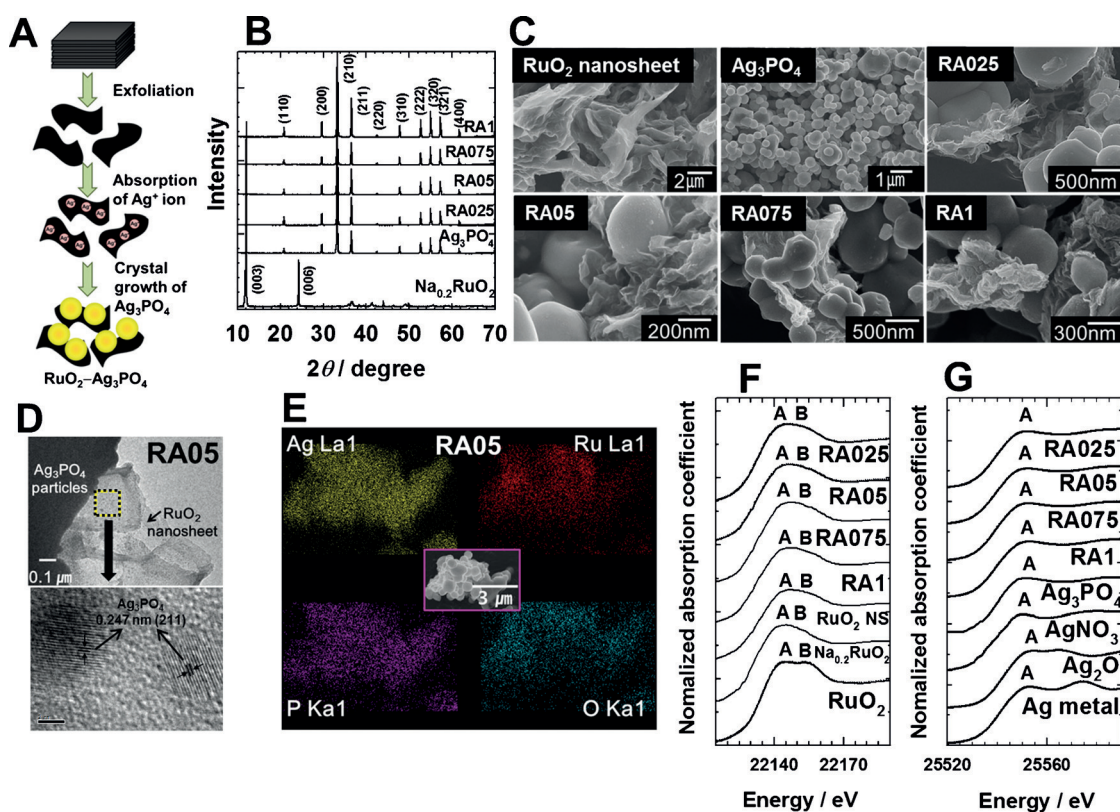


Figure 1. A) Exfoliation and crystal growth route to the RA nanohybrid. Powder XRD patterns (B), FE-SEM images (C), HR-TEM images (D), EDS elemental maps (E), and Ru K-edge (F) and Ag K-edge (G) XANES spectra of the RA nanohybrids and references.

nanoparticles immobilized on the RuO₂ NS (Figure 1D). EDS elemental mapping analysis provides clear evidence for the nanoscale mixing between these two components (Figure 1E). N₂ adsorption-desorption isotherm analysis demonstrates only a weak N₂ adsorption for all the RA nanohybrids, thus suggesting negligible contribution of surface expansion to the evolution of photocatalytic activity upon RuO₂ addition (see Figure S2). The maintenance of a layered RuO₂ structure upon hybridization with Ag₃PO₄ is evidenced by the Ru K-edge X-ray absorption near-edge structure (XANES) spectroscopy showing nearly identical features for the present RA nanohybrids and layered RuO₂ (Figure 1F). Similarly, all the RA nanohybrids commonly exhibit Ag K-edge XANES features which are nearly identical to that of Ag₃PO₄, thus reflecting the negligible effect of RuO₂ incorporation on the chemical bonding nature of Ag₃PO₄ (Figure 1G). The diffuse reflectance UV/Vis spectra in Figure 2A demonstrate that the increase of RuO₂ content in the RA nanohybrids enhances the absorption of visible light, thus confirming the successful incorporation of metallic RuO₂ NSs. As plotted in Figure 2B, the hybridization with RuO₂ NSs depresses the photoluminescence (PL) signal of Ag₃PO₄, thus underscoring the notable depression of the electron-hole recombination caused by CT from Ag₃PO₄ to RuO₂ (Figure 2C).

As can be seen clearly from Figure 2D, all the RA nanohybrids display photocatalytic activity, for visible-light-induced O₂ evolution ($\lambda > 400$ nm), which is higher than that of pure Ag₃PO₄, and underscores the beneficial effect of

RuO₂ incorporation on the photocatalytic activity of Ag₃PO₄. Among the present materials, the RA05 nanohybrid with the intermediate RuO₂/Ag₃PO₄ ratio has the highest photocatalytic activity with a rate of 0.975 mmol h⁻¹ g⁻¹, which is much higher than that of unhybridized Ag₃PO₄ (0.597 mmol h⁻¹ g⁻¹). Similarly, all the RA nanohybrids can induce an efficient decomposition of methylene blue (MB) under visible-light ($\lambda > 420$ nm) irradiation. The rate of MB degradation is much faster for the RA nanohybrids than for the unhybridized Ag₃PO₄, thus confirming the beneficial role of RuO₂ NSs (Figure 2E). Taking into account the high electrical conductivity of the RuO₂ NS, this material is supposed to act as electron reservoir, conducting pathway, and cocatalyst in the present nanohybrid, much like the role of graphene in the graphene-based hybrid photocatalyst.^[9] To investigate the relative efficiency of RuO₂ NS over the widely-used rG-O NS, the rG-O-Ag₃PO₄ nanohybrid with the rG-O/Ag₃PO₄ ratio of 0.05 wt% was also prepared by the same synthetic procedure (the obtained material is denoted as GA05). The hybridization between rG-O and Ag₃PO₄ is confirmed by powder XRD analysis and UV/Vis spectroscopy (see Figures S3 and S4). The hybridization of Ag₃PO₄ with rG-O leads to the depression of PL intensity, and is however less effective than that with RuO₂ NS (see Figure S5). This result provides strong evidence for a better role of RuO₂ NSs as a hybridization matrix than rG-O in enhancing the internal CT with Ag₃PO₄. As plotted in Figures 2D and E, the GA05 nanohybrid shows a lower photocatalytic activity for both O₂ evolution and MB degradation than does the RA05 nano-

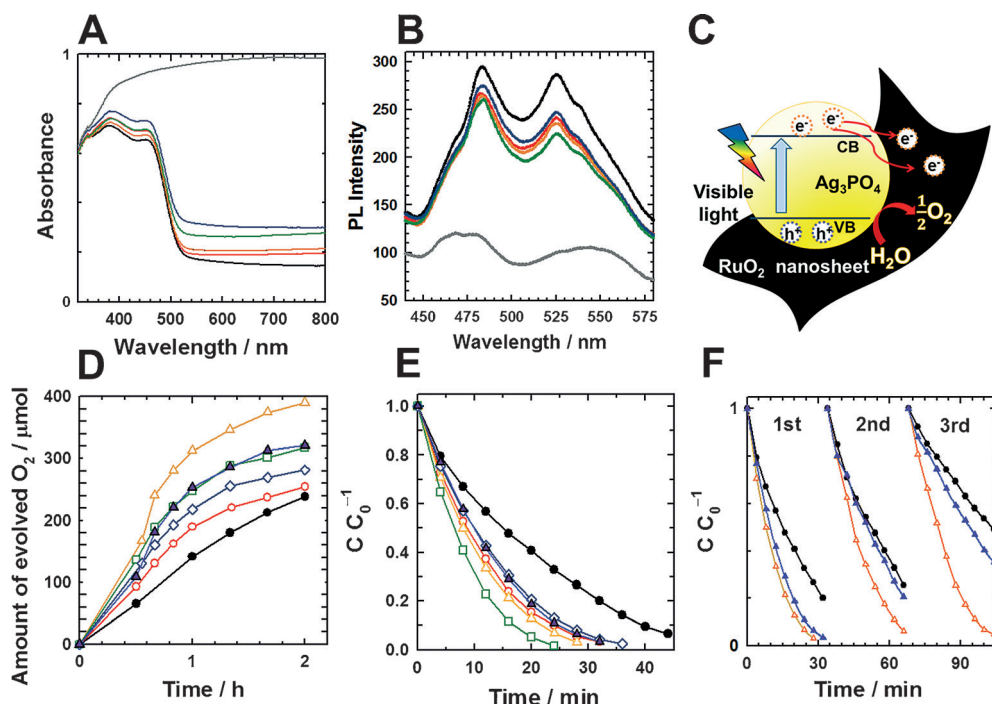


Figure 2. Diffuse reflectance UV/Vis spectra (A), PL spectra (B), visible-light-induced O_2 evolution (D), visible-light-induced MB decomposition (E), and repeated tests (F) of photocatalytic activities of the pristine $\text{Na}_0.2\text{RuO}_2$ (gray), Ag_3PO_4 (black), RA025 (red), RA05 (orange), RA075 (green), RA1 (blue), and GA05 (purple). C) Model for internal electron transfer in the RA nanohybrids.

hybrid, thus highlighting the inferior role of rG-O over RuO_2 NSs in improving the photocatalytic activity of Ag_3PO_4 . The hybridization effect on the photostability of Ag_3PO_4 was also tested with three successive photodegradations of MB (Figure 2F). In contrast to bulk Ag_3PO_4 which shows a marked degradation in photocatalytic activity, the RA05 nanohybrid displays only a negligible change. The improved photostability of Ag_3PO_4 upon the RuO_2 incorporation is attributable to an efficient migration of photoexcited electrons from Ag_3PO_4 to the RuO_2 NS, thus leading to the depression of the photoreduction of Ag^+ cation (Figure 2C). Such a beneficial effect of RuO_2 NS addition is more efficient than rG-O addition (Figure 2F). The present findings clearly demonstrate that the hybridization with RuO_2 NSs is fairly powerful for enhancing the photocatalytic activity and photostability of metal oxosalt.

To understand the better performance of the RuO_2 NSs than rG-O, their surface was examined with contact angle measurements (see Figure S6). While a wide contact angle of 84.1° is observable for the freestanding membrane of the rG-O NS, the RuO_2 membrane shows a much smaller contact angle of 26.6° , thus reflecting the higher surface hydrophilicity of RuO_2 than rG-O. The hydrophilic nature of the RuO_2 NS is responsible for more efficient chemical interactions and internal CT with polar Ag_3PO_4 particles, thus leading to the higher photocatalytic activity and photostability of the RA nanohybrid relative to that of GA. Ab initio DFT calculations further elucidate the atomic and electronic details of the hybrid interfaces between RuO_2 /rG-O and Ag_3PO_4 . First, we calculated the electronic band structure and density of states

(DOS) of the isolated monolayer of RuO_2 , and the data suggested that the major electronic conducting pathway within RuO_2 monolayer is by Ru atoms (Figure 3A). After the DFT optimization, we found the formation of Ag–O bonds at the RuO_2 / Ag_3PO_4 interface, thus inferring the strong hybridization between RuO_2 and Ag_3PO_4 surfaces (Figure 3B). The distance between the layer and the surface is $2.2 \text{ \AA}$ (cf. Ag–O van der Waals (vdW) distance = $3.2 \text{ \AA}$). This distance is in stark contrast to the graphene/ Ag_3PO_4 interface, which shows a marginal geometrical change from their isolated structures (Figure 3C) with the atomically flat graphene sheet and a contact distance of $3.2 \text{ \AA}$ (cf. C–O vdW distance = $3.2 \text{ \AA}$), thus indicating the covalent nature of RuO_2 /

Ag_3PO_4 interface and the vdW-type nature of the graphene/ Ag_3PO_4 interface. The stronger interfacial hybridization of RuO_2 / Ag_3PO_4 over graphene/ Ag_3PO_4 is consequently reflected by the larger CT at the interface. As the charge density differences show in Figures 3D and E, the RuO_2 / Ag_3PO_4 interface exhibits around tenfold more profound CT compared with that of graphene/ Ag_3PO_4 . The CT direction for RuO_2 / Ag_3PO_4 is opposite for that of graphene/ Ag_3PO_4 , that is, CT from Ag_3PO_4 to RuO_2 versus CT from graphene to Ag_3PO_4 . The former case yields a local electric field from Ag_3PO_4 to RuO_2 and helps the separation of excited electron from Ag_3PO_4 to the hybridization matrix while leaving a hole in the Ag_3PO_4 . We also found that CT at the RuO_2 / Ag_3PO_4 interface occurs for the entire RuO_2 sheet and for several atomic layers of the Ag_3PO_4 surface, while CT at the graphene/ Ag_3PO_4 interface mostly occurs between graphene and only the top layer of Ag_3PO_4 surface. Our DFT results clearly indicate the existence of a much stronger donor–acceptor interaction in the RuO_2 / Ag_3PO_4 interface, thus helping the excited electron–hole separation. A strong hybridization between the RuO_2 nanosheet and Ag_3PO_4 is confirmed by the observation of micro-Raman feature of the Ag–O interaction (see Figure S7).

The universal merit of RuO_2 hybridization in improving the photocatalytic activity of a semiconductor is further evidenced by the comparative investigation for the nanohybrids of RuO_2 -CdS and rG-O-CdS with the RuO_2 /CdS or rG-O/CdS ratio of 0.5 wt % (see Figures S8 and S9). As presented in Figure 4, the hybridization with RuO_2 NSs is much more effective in improving the visible light ($\lambda >$

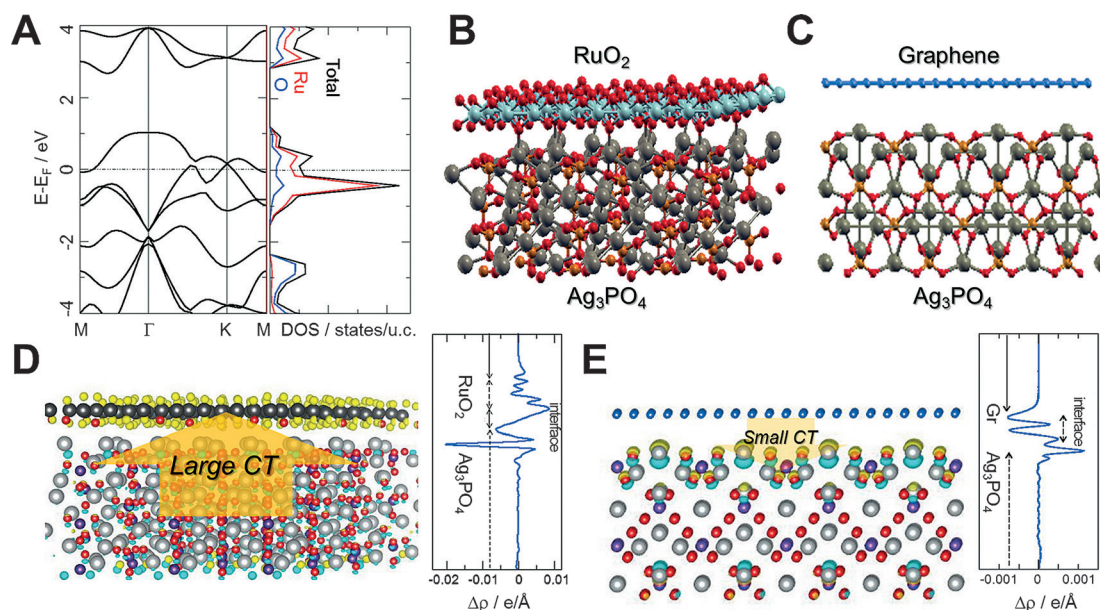


Figure 3. A) Electronic band structure and density of states of the isolated RuO_2 sheet. Side-views of DFT optimized atomistic structures of $\text{RuO}_2/\text{Ag}_3\text{PO}_4(111)$ interface (covalent type; B) and C) graphene/ $\text{Ag}_3\text{PO}_4(100)$ interface (vdW type; C). Ag gray, O red, P orange, C blue, and Ru aquamarine. Charge density differences (ρ) of the $\text{RuO}_2/\text{Ag}_3\text{PO}_4$ (D) and graphene/ Ag_3PO_4 (E) hybrid interface. In the left panels, charge density differences are shown three-dimensionally; the yellow and cyan regions represent charge accumulation and depletion, respectively. In the right panels, the planar-averaged charge density differences are plotted along the surface normal direction (chosen as the z-direction).

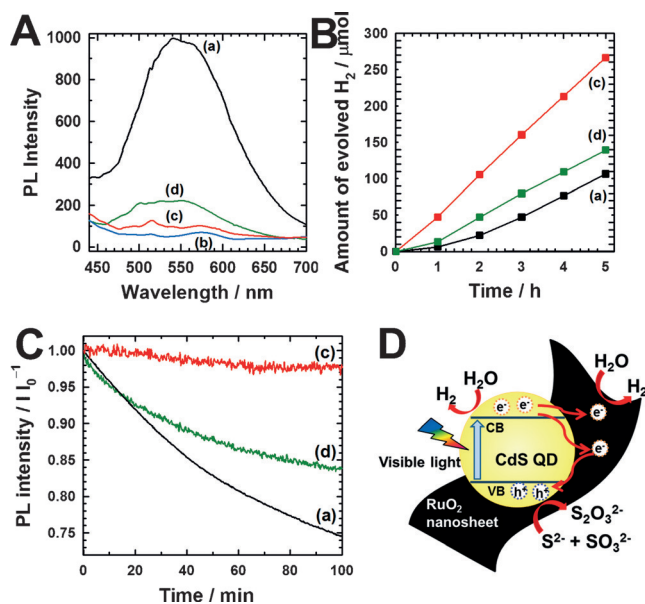


Figure 4. PL spectra (A), visible-light-induced H_2 generation (B), and photostability test (C) of CdS QD (a), $\text{Na}_{0.2}\text{RuO}_2$ (b), RuO_2 -CdS nanohybrid (c), and rG-O-CdS nanohybrid (d). D) Model for internal electron transfer in the RuO_2 -CdS nanohybrid.

420 nm) photocatalytic activity of CdS quantum dots for H_2 production and photocurrent generation (see Figure S10), and its photostability, and is ascribable to the depression of the electron-hole recombination. The importance of the very thin exfoliated RuO_2 nanosheet in improving the photocatalyst activity of the semiconductor is evidenced by the efficient generation of H_2 by the RuO_2 -CdS nanohybrid

relative to that of the nanohybrid of CdS and unexfoliated $\text{Na}_{0.2}\text{RuO}_2$ material (see Figure S11). This result highlights a beneficial role of the RuO_2 NS in exploring highly efficient hybrid photocatalyst. In conclusion, we have developed a novel universal hybridization route to efficient photocatalyst materials by employing exfoliated RuO_2 2D NSs as a conducting hybridization matrix. Despite the lower electrical conductivity of RuO_2 (833 Scm^{-1}) relative to graphene (6000 Scm^{-1}),^[10,11] the hybridization with hydrophilic RuO_2 NSs is more effective in improving the photocatalytic activity and photostability of semiconductor nanocrystals compared with that with hydrophobic rG-O. This result is attributable to more efficient CT between RuO_2 and semiconductors, thus highlighting the importance of a chemical interaction between the hybridized components in optimizing the photocatalyst performance of nanohybrids. The present RuO_2 -based nanohybrids show higher photocatalytic activity than do the well-known N- and Pt-doped TiO_2 materials, thus confirming the promising photocatalyst performance of the present nanohybrids (see Figure S12). Even though ruthenium is more expensive than carbon, this element is 20 times cheaper than platinum, which is widely used as a cocatalyst for photocatalyst systems.^[12] Taking into account the fact that the hybridization with graphene has led to a great deal of research devoted to the graphene-based hybrid photocatalysts,^[9] the present study should lead to new opportunities for the exploration of new RuO_2 NS-based hybrid photocatalysts.

Acknowledgments

This work was supported by the Global Frontier R&D Program (2013-073298 and 2013M3A6B1078884) on Center

for Hybrid Interface Materials (HIM) from the National Research Foundation of Korea (NRF) on a grant funded by the Korea government (MSIP) (No. NRF-2014R1A2A1A10052809). The experiments at PAL were supported in part by MOST and POSTECH.

Keywords: conducting materials · graphene · nanostructures · photocatalysis · semiconductors

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 8546–8550
Angew. Chem. **2016**, *128*, 8688–8692

-
- [1] J. Tao, T. Luttrell, M. Batzill, *Nat. Chem.* **2011**, *3*, 296–300.
[2] B. P. Bastakoti, Y. Li, M. Imura, N. Miyamoto, T. Nakato, T. Sasaki, Y. Yamauchi, *Angew. Chem. Int. Ed.* **2015**, *54*, 4222–4225; *Angew. Chem.* **2015**, *127*, 4296–4299.
[3] M. Osada, T. Sasaki, *Adv. Mater.* **2012**, *24*, 210–228.
[4] T. Sasaki, Y. Ebina, Y. Kitami, M. Watanabe, *J. Phys. Chem. B* **2001**, *105*, 6116–6121.
[5] C. N. R. Rao, H. S. S. R. Matte, U. Maitra, *Angew. Chem. Int. Ed.* **2013**, *52*, 13162–13185; *Angew. Chem.* **2013**, *125*, 13400–13424.
[6] Z. Zeng, T. Sun, J. Zhu, Z. Huang, Z. Yin, G. Lu, Z. Fan, Q. Yan, H. H. Hng, H. Zhang, *Angew. Chem. Int. Ed.* **2012**, *51*, 9052–9056; *Angew. Chem.* **2012**, *124*, 9186–9190.
[7] Q. J. Xiang, J. G. Yu, M. Jaroniec, *Nanoscale* **2011**, *3*, 3670–3678.
[8] K. Fukuda, T. Saida, J. Sato, M. Yonezawa, Y. Takasu, W. Sugimoto, *Inorg. Chem.* **2010**, *49*, 4391–4393.
[9] Q. Xiang, B. Cheng, J. Yu, *Angew. Chem. Int. Ed.* **2015**, *54*, 11350–11366; *Angew. Chem.* **2015**, *127*, 11508–11524.
[10] J. Sato, H. Sato, M. Kimura, K. Fukuda, W. Sugimoto, *Langmuir* **2010**, *26*, 18049–18054.
[11] X. Du, I. Skachko, A. Barker, E. Y. Andrei, *Nat. Nanotechnol.* **2008**, *3*, 491–495.
[12] InvestmentMine. (2016, Jan. 29). Retrieved from <http://www.infomind.com/investment/metal-prices>.
-

Received: February 11, 2016

Revised: April 19, 2016

Published online: May 31, 2016