Supporting Information Available

Reduced Graphene Oxide as a Solid-state Electron Mediator in Z-scheme Photocatalytic Water Splitting under visible light

Akihide Iwase,[1] Yun Hau Ng,[1] Yoshimi Ishiguro,[2] Akihiko Kudo,[2] Rose Amal[1, *]

1: ARC Centre of Excellence for Functional Nanomaterials, School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052 Australia

2: Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601 JAPAN

Experimental Sections

Preparation of graphene oxide, $Ru/SrTiO_3$, and $BiVO_4$

Graphene oxide was synthesized from the commercially obtained graphite powder using Hummers' method.[1] The graphite was oxidized to graphene oxide by $KMnO_4$ in a sulfuric acid solution containing $NaNO_3$. The obtained graphene oxide was collected as dark brown powder by filtration. XPS measurements only revealed carbon and oxygen elements on the graphene oxide .No Mn species were detected.

$SrTiO_3$ doped with Rh ($SrTiO_3$:Rh) powder was prepared by a solid-state reaction as previously reported.[2] The starting materials TiO_2 (Aldrich; 99.9%), $SrCO_3$ (Alfa Aesar; 99%), and Rh_2O_3 (Aldrich; 99.8%) were mixed in a mortar according to the ratio Sr:Ti:Rh=1.03:1:0.01. The mixture was calcined at 1423K for 10 hours in air using an alumina crucible. Ru-cocatalyst (0.7 wt%), which works as an active site for H_2 evolution, was loaded on the $SrTiO_3$:Rh by photodeposition from an aqueous methanol solution containing $RuCl_3 \bullet nH_2O$ (Sigma-Aldrich; 38-40% as Rh). The Ru cocatalyst-loaded $SrTiO_3$:Rh ($Ru/SrTiO_3$:Rh) powder was collected by filtration and washed with distilled water before drying. $BiVO_4$ powder was synthesized via a solid-liquid reaction at room temperature.[3] Starting materials of $Bi(NO)_3 \bullet 5H_2O$ (Sigma-Aldrich; 98%) and V_2O_5(Aldrich; 99.6%) were stirred in 0.75 mol L^{-1} of an aqueous nitric acid solution (50 mL) for 48 hours. The molar ratio of vanadium to bismuth in the starting materials was 1:1. Obtained $BiVO_4$ powder was collected by filtration and washed with distilled water before drying.

Reduction of graphene oxide

Photoreduced graphene oxide with $Ru/SrTiO_3$:Rh and $BiVO_4$ (PRGO/$Ru/SrTiO_3$:Rh and PRGO/$BiVO_4$) were prepared by photocatalytic reduction as previously reported.[4–7] Graphene oxide (5 wt% of

photocatalyst) and photocatalyst ($Ru/SrTiO_3$:Rh and $BiVO_4$) powders were suspended in 50 vol% of aqueous methanol solution (30mL). The suspensions were stirred and bubbled with Ar gas during visible light irradiation for 2 hours. As a reference, chemical reduced graphene oxide was also prepared using hydrazine.

Characterization

The crystal phase of the obtained powders was confirmed by X-ray diffraction (Philips; Xpert Multipurpose X-ray Diffraction System). Photocatalysts were observed using an optical microscope (LEICA; DM 2500M) and a scanning electron microscope (Hitachi; S4500). Photocatalyst powders suspended in water with pH adjusted using H_2SO_4 were dropped on a glass slide and observed using the optical microscope without drying. The suspended powders were also dropped on an aluminum foil and subsequently dried for SEM observation. The oxidation states of graphene were studied using X-ray photoelectron spectroscopy (VG; ESCALab220i-XL) with monochromated Al Kα radiation ($h\nu$ = 1486.6 eV). To measure the conductivity (expressed as sheet resistance) of graphite, graphene oxide and photoreduced graphene oxide, the suspension of each powder in ethanol solution was drop casted onto glass fiber membrane to form thin films with surface density of 2 mg cm^{-2}. Sheet resistance measurement of graphite, graphene oxide and photoreduced graphene oxide was performed on a JANDEL RM-3 four-point probe.

Photocatalytic water splitting

Photocatalytic water splitting was carried out in a gas-closed-circulation system shown in Figure 11 in Ref 8. In this system, the gas sampling port from the reactor is directly connected to a gas chromatograph (TCD, MS-5A, Ar carrier gas) for measuring online the evolved H_2 and O_2. Photocatalyst powders (0.03 g) were dispersed in water (120 mL) and its pH was adjusted with H_2SO_4 in a top irradiation cell with a Pyrex window. The photocatalyst was irradiated using a 300-W Xe lamp (Perkin Elmer, CERMAX PE-300BBF). Visible light was controlled by a cutoff filter (Schott; GG420).

References

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Reliability of activity data

In our closed gas circulation water splitting system, the gas sampling port from the reactor is directly connected to a gas chromatograph for measuring online the evolved gas. Therefore, the experimental errors are drastically minimized compared to those carried out using a syringe to draw the gases.

For selected samples which we think the activity results are critical for the findings of this paper, few times measurements of the fresh samples were carried out. For example, (i) $Ru/SrTiO_3$:Rh and PRGO/$BiVO_4$ sample, (Entry 8 in Table 1), the measured activities are (H_2: 9.4 μmol h^{-1}, O_2: 4.4 μmol h^{-1}), (11.2, 5.5), and (10.8, 5.5), and (ii) for $Ru/SrTiO_3$:Rh and $BiVO_4$ (Entry 5, Table 1), the measured activities are (H_2:3.7 μmol h^{-1}, O_2: 1.9 μmol h^{-1}) and (4.9, 2.2).

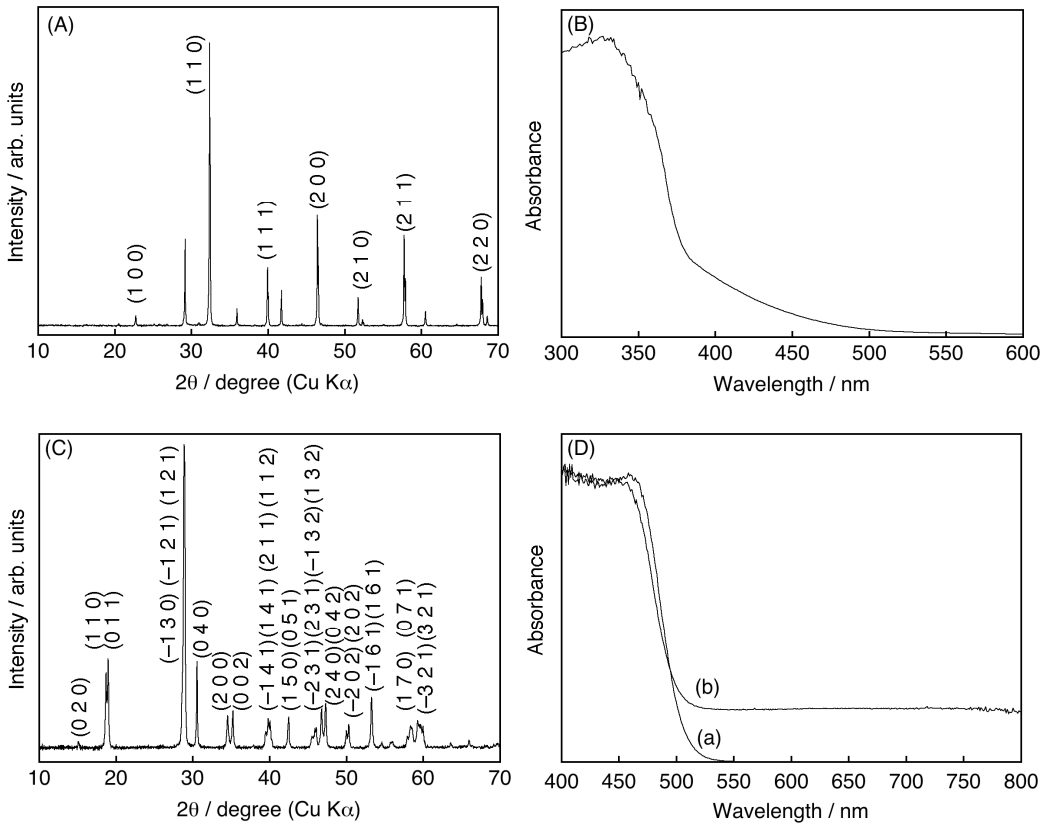

Figure S1. XRD patterns of (A) $SrTiO_3$:Rh and (C) $BiVO_4$, and diffuse reflectance spectra of (B) $SrTiO_3$:Rh with H_2-reduction and (D)-(a) $BiVO_4$ and (b) photoreduced graphene oxide/$BiVO_4$.

From XRD patterns, (A) and (C), we confirmed that $SrTiO_3$:Rh and $BiVO_4$ photocatalysts were obtained. $SrTiO_3$:Rh includes unknown impurity phase. UV-vis spectra, (C) and (D-a), indicates that both $SrTiO_3$:Rh with H_2-reduction (EG: 2.3 eV) and $BiVO_4$ (BG: 2.4 eV) respond to visible light. It is known that the the Rh ions in $SrTiO_3$:Rh is reduced during photocatalysis and contributes to H_2 evolution.[1]

Based on the UV-vis spectrum of photoreduced graphene oxide (PRGO)/$BiVO_4$, the black-colored PRGO associated with an increase in the base line of absorption would have absorbed the incident light and reduced the amount of photons in exciting the $BiVO_4$ and Ru/$SrTiO_3$:Rh. Despite this negative effect, the observation of triple enhancement in water splitting activity strengthens the constructive effect of PRGO in shuttling the electrons in Z-scheme system.

References

(1) Konta, R.; Ishii, T.; Kato, H.; Kudo, A. *J. Phys. Chem. B* **2004**, *108*, 8992.

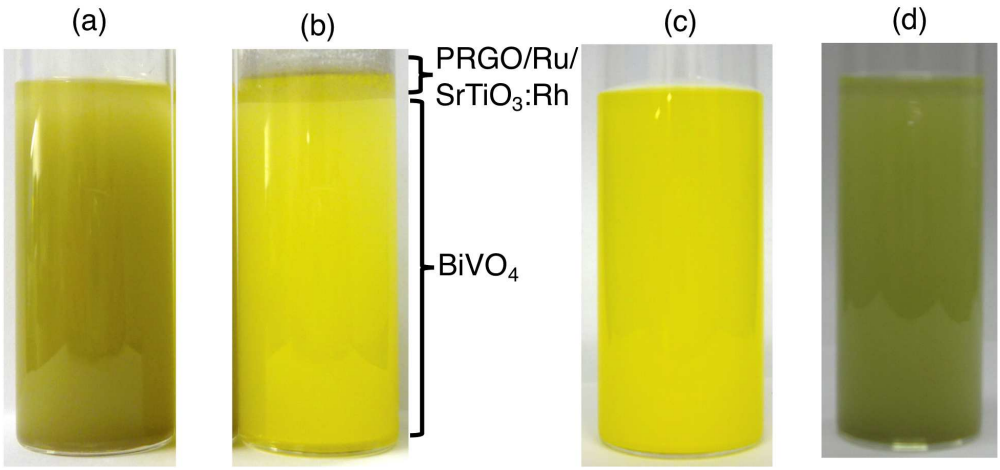

Figure S2. Photograph of (a) $Ru/SrTiO_3$:Rh and $BiVO_4$ and (b) photoreduced graphene oxide (PRGO)/$Ru/SrTiO_3$:Rh and $BiVO_4$, (c) $BiVO_4$, and (d) $Ru/SrTiO_3$:Rh and PRGO/$BiVO_4$suspended in water at pH 3.5.

Figure S2 (a) indicates bare $Ru/SrTiO_3$:Rh and $BiVO_4$ particles can well disperse in water. In Figure S2 (b), gray layer of PRGO/$Ru/SrTiO_3$:Rh is observed on the top of solution, while the most part of solution shows bright yellow being the same as the suspension of the pure $BiVO_4$ shown in Figure S2 (c), clearly indicating the separation of PRGO/$Ru/SrTiO_3$:Rh from the solution strong hydrophobicity of the PRGO/$Ru/SrTiO_3$:Rh particles. In contrast, Figure S2 (d) shows that both $Ru/SrTiO_3$:Rh and PRGO/$BiVO_4$ particles, that this combination gives the most highest activity, dispersed well in water.

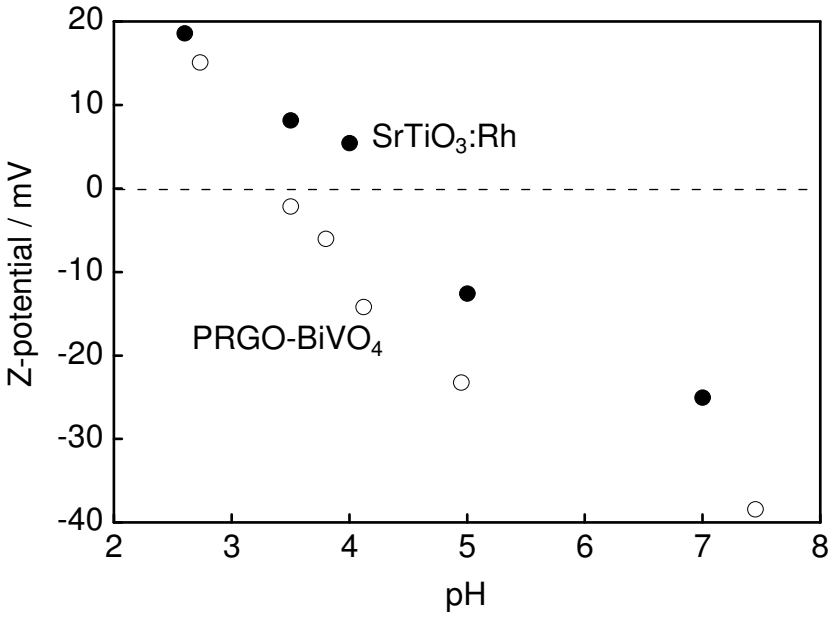

Figure S3. Z-potential of $SrTiO_3$:Rh (closed mark) and photoreduced graphene oxide/$BiVO_4$ (open mark).

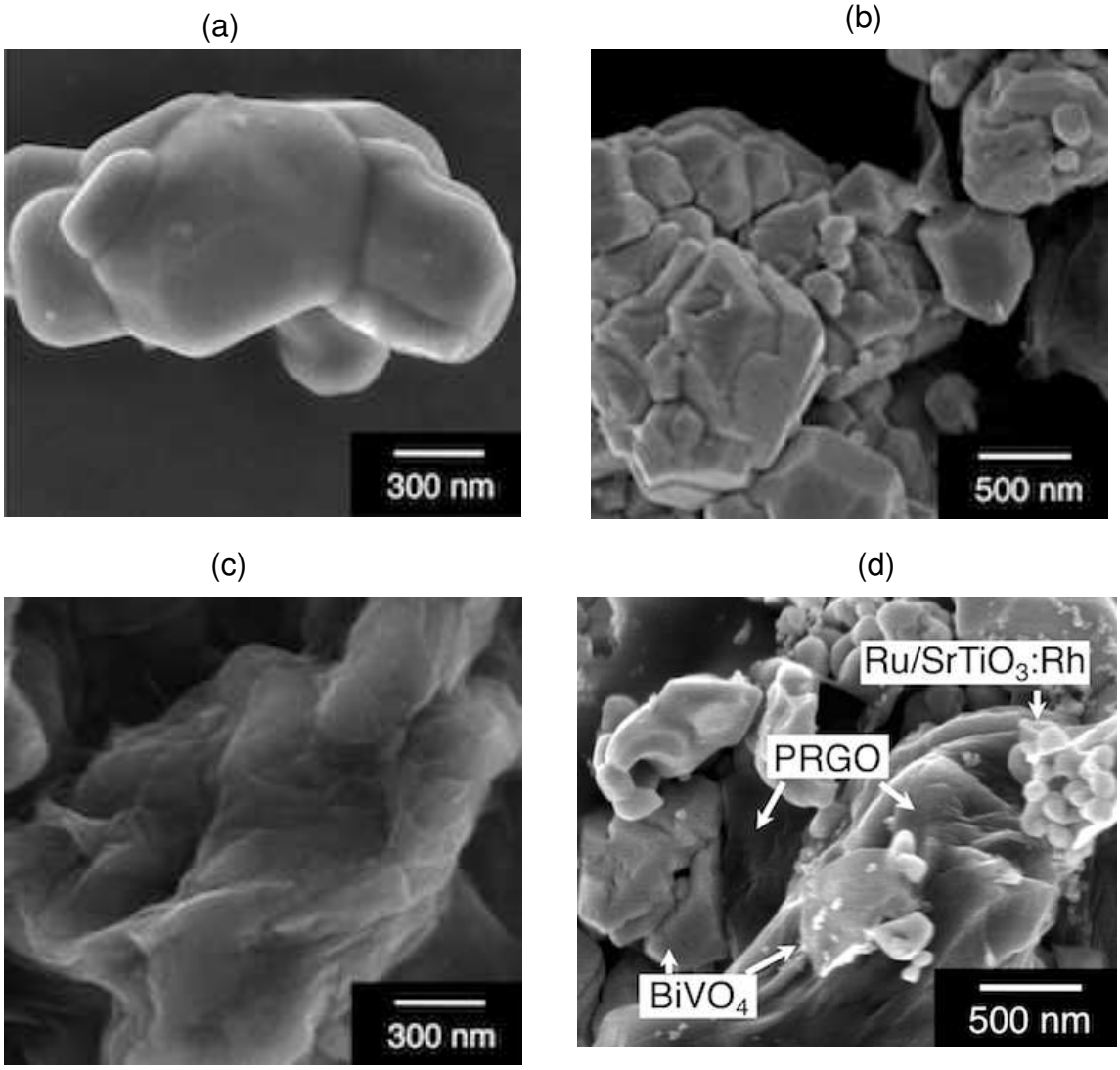

Figure S4. SEM images of (a) $SrTiO_3$:Rh, (b) $BiVO_4$, (c) graphene oxide, and (d) Ru/$SrTiO_3$:Rh and photoreduced graphene oxide/$BiVO_4$. The samples for (d) was prepared by drop-casting the suspended powders of Ru/$SrTiO_3$:Rh and photoreduced graphene oxide/$BiVO_4$ in water at pH 3.5 on a SEM sample folder and drying.