Supplementary Information

Production of water-dispersible reduced graphene oxide without stabilizers using liquid-phase photoreduction

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Experimental Section

Preparation of graphene oxide solution

Graphene oxide (GO) was prepared from a graphite powder (Wako Ltd.) by a modified Hummers' method reported by our previous report.[1] First, the graphite powder was oxidized by $NaNO_3$, H_2SO_4, $KMnO_4$ and H_2O_2. The resulting suspension was washed several times using dilute hydrochloric acid (5% in water) and distilled water and then dried in an oven at 50 °C for a day. The resultant graphite oxide was exfoliated in water by ultrasonication (SND Co., Ltd, US-10NS) for 2 h. Finally, a GO solution (12.3 g/l) was obtained by centrifuging the produced GO and graphite oxide mixture to separate GO from graphite oxide.

Tuning pH of GO solution

A pH of GO solution was tuned using 2.5% ammonia solution. Ammonia, which is gas state under ambient conditions, can be easily removed from GO after photoreduction unlike in the case of using solid-state agents such as NaOH and phosphate buffer. We prepared three kinds of alkaline GO solutions with pH 8.02, 8.96 and 9.94 by adding 2.5% ammonia solution to GO solution diluted by 200 times. Another alkaline GO solution with pH 9.94 was prepared using 0.1 M NaOH solution.

Photoreduction of GO solution

Photoreduction of GO solution was performed using a Xe lamp (USHIO SX-UI500XQ, 500 W) under vacuum conditions (-80 – -85 kPa) for 30 h. A 50 ml quartz cell was used as the reaction chamber. We also curried out photoreduction with N_2 bubbling and have obtained the same result with a vacuum condition. About 0.80 g and 0.64 g of al-rGO and n-rGO were obtained from 1 g of graphite powder, respectively. Because al-rGO and n-rGO contained 13.9 and 15.5 atm% of oxygen atoms (Fig. 4 in the main text), the yields of each rGO samples were 71 and 56 %, respectively. The higher yield of al-rGO than that of n-rGO is attributed to the reduction of GO without decomposition into CO_2 under alkaline condition.

Characterizations

The morphology of the GO and rGO were investigated by atomic force microscopy (AFM; Bruker, Digital Instruments Nanoscope V). X-ray photoelectron spectroscopy (XPS; Thermo Scientific, Sigma Probe) was used to analyze the functional groups in the GO and rGO nanosheets. The gases generated in the reaction cell were determined by online gas chromatography (Shimadzu, GC-8A).

Electrical conductivity measurement

The electrical conductivities of GO, n-rGO, al-rGO and rGO reduced by hydrazine (h-rGO) were measured by four-probe DC method using a potentiostat with a function generator (IVIUM TECHNOLOGIES, CompactStat). h-rGO was prepared by mixing 10 ml of GO solution diluted by 10 times and 0.5 ml hydrazine monohydrate and leaving for 30 h. We employed a conventional vacuum filtration method to make GO and rGO films. The thickness of GO, n-rGO, al-rGO and h-rGO films were 0.015, 0.015, 0.015 and 0.011 mm, respectively.

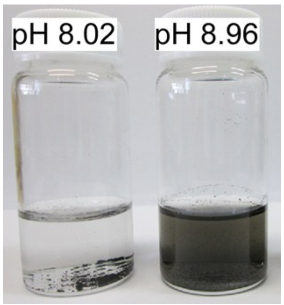

Fig. S1 Photograph of the rGO solution prepared by photoreduction in pH 8.02 and 8.96. rGO solution prepared by photoreduction in pH 8.02 strongly aggregated as well as n-rGO solution (Fig. 1 in the main text). Although aggregation occurred in the case of rGO solution prepared by photoreduction in pH 8.96, the degree of aggregation is lower than that in pH 8.02.

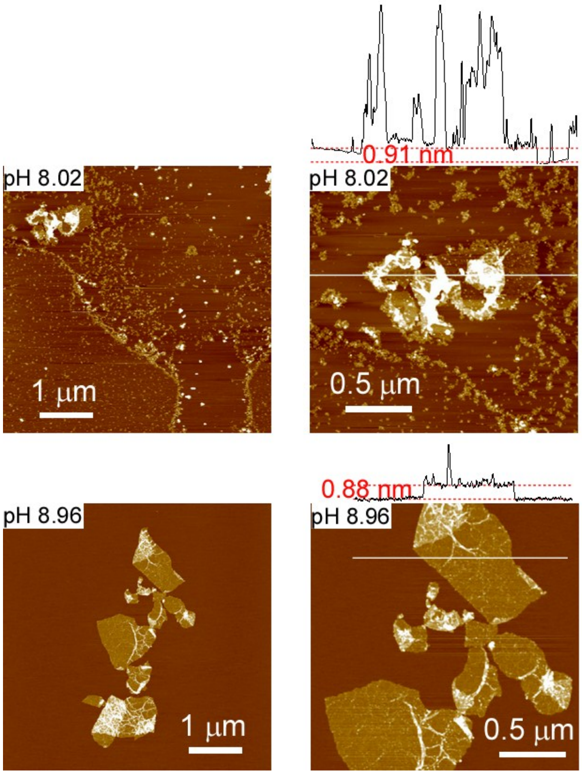

Fig. 2 AFM images of the rGO prepared by photoreduction in pH 8.02 and 8.96. Very few single-layer nanosheets and many small rubbles of rGO were observed in rGO sample prepared by photoreduction in pH 8.02. On the other hand, many single-layer nanosheets were observed in rGO sample prepared by photoreduction in pH 8.96 as well as the case of al-rGO (Fig. 2c in the main text). However, rGO nanosheets reduced in pH 8.96 have a relatively rougher surface than al-rGO nanosheets, which means that low decomposition occurred during photoreduction in pH 8.96. Following these results, there is likely a turning point determining the aggregation and decomposition of GO between pH 8.02 and 8.96.

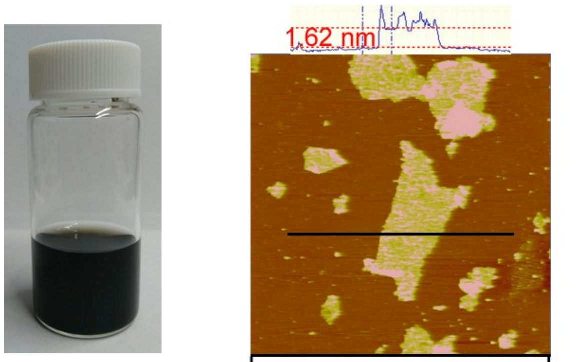

Fig. S3 Photograph and AFM image of rGO nanosheets prepared by photoreduction with NaOH. Well-dispersed rGO could be also obtained in the case of using NaOH instead of ammonia. However, rGO nanosheets prepared by photoreduction with NaOH had thick thickness, which indicate that solid-state NaOH remain on rGO nanosheets.

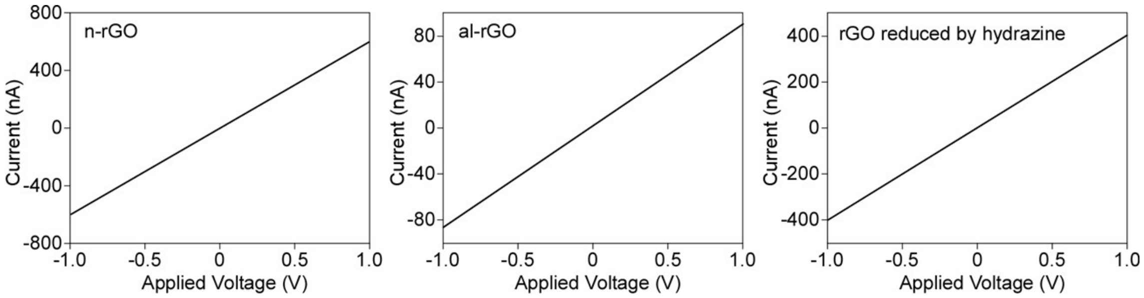

Fig. S4 *I-V* curves of the n-rGO, al-rGO and h-rGO films obtained by four-probe DC measurement. The thickness of n-rGO, al-rGO and h-rGO films were 0.015, 0.015 and 0.011 mm, respectively. The current through the GO film was undetectable due to the extremely low conductivity of GO.

Table S1 The elemental composition of pristine GO, n-rGO and al-rGO determined by XPS.

	C	O	N	S	Na	Sn	K
GO	64.9	30.7	2.4	2.4	0.4	N/A	N/A
n-rGO	71.5	27.9	2.8	N/A	N/A	0.6	N/A
al-rGO	74.5	22.7	N/A	N/A	N/A	N/A	0.4

Table S2 The electrical conductivities of GO n-rGO, al-rGO and h-rGO films calculated from *I-V* curve (Fig. S4).

	Electrical conductivity (S/cm)
GO	N/A
n-rGO	2.4×10^{-4}
al-rGO	4.8×10^{-5}
h-rGO	2.5×10^{-4}

Reference

R1. Y. Matsumoto, M. Koinuma, S. Ida, S. Hayami, T. Taniguchi, K. Hatakeyama, H. Tateishi, Y. Watanabe and S. Amano, *J. Phys. Chem. C*, 2011, **115**, 19280-19286.