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Supporting Information

Cerium-Doped Gehlenite Supporting Silver/Silver Chloride for Continuous Photocatalysis

Haoyi Wu, Wen-Qin Peng, Zheng-Ming Wang,* Kazuhide Koike
Environmental Management Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8569, Ibaraki, Japan

*Corresponding author: zm-wang@aist.go.jp

1. Water-resisting properties of LLPs

The water resisting properties of the prepared $Ca_2Al_2SiO_7$: Ce^{3+} LLPs (the G sample) were examined and compared with a commercial violet-emitting LLP, V300M (LumiNova V series, Nemoto & Co., Ltd.) by the following procedures: 20 mg powders of the prepared samples or V300M were dispersed in 10 mL deionized water under magnetic stirring for 4 and 24 hours, after which the powders were collected by centrifuging and drying. The structural and luminescent properties of each sample were recorded and compared with the fresh sample and the commercial one.

As shown in Figure S1, after immersion in water for 4 hours, the peak at 798 cm^{-1} due to the Al-O stretching mode is weakened and a new peak at 1430 cm^{-1} attributable to carbonate species appears for the G sample. The FT-IR spectrum of the immersed G sample is very similar to that of G10A1. On the other hand, the crystal structure of G is almost unchanged after immersion in water for 24 hours, as evidenced by the XRD patterns (Figure S2). Thus, the structural change induced by water immersion is very limited for the G sample though it leads to ~30% reduction in luminescence intensity. As the XRD patterns confirm the weakening of the aluminate impurity structure (annotated with ര) and the appearance of carbonate species (annotated with ❋), we ascribed the partial structural change in water to the decomposition of the aluminate impurity or the collapse of a little part of Al-O bond in the G framework.

In comparison with the G sample synthesized herein, the Al-based commercial violet-emitting LLP does not resist against water at all though it shows very high emission brightness in air. Its structure thoroughly changes and its photo-emitting ability is completely lost after immersion in water for 4 hours (Figure S3).

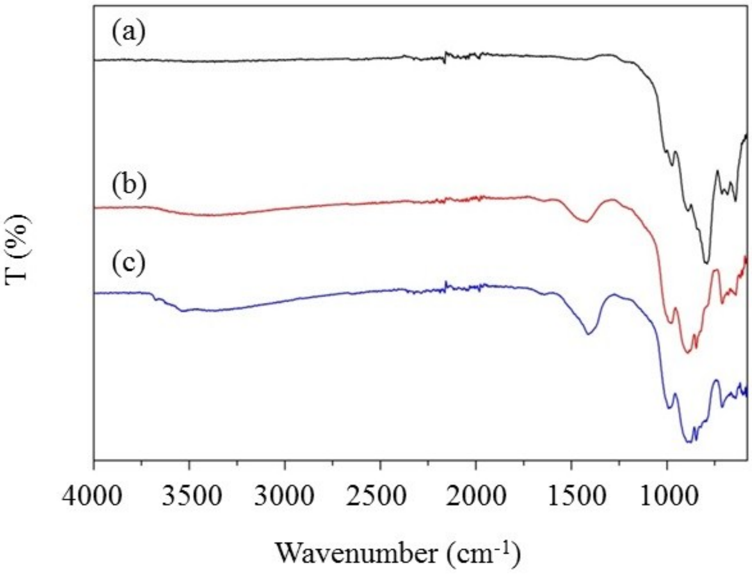

Figure S1. FTIR spectra of (a) G, (b) G immersed in water for 4 hours, and (c) G10A1.

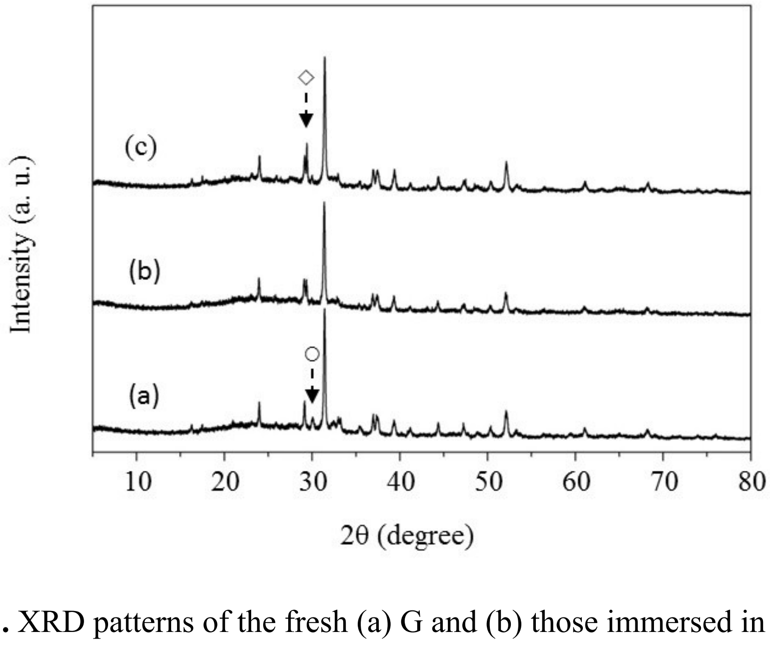

Figure S2. XRD patterns of the fresh (a) G and (b) those immersed in water for 4 and (c) 24 hours.

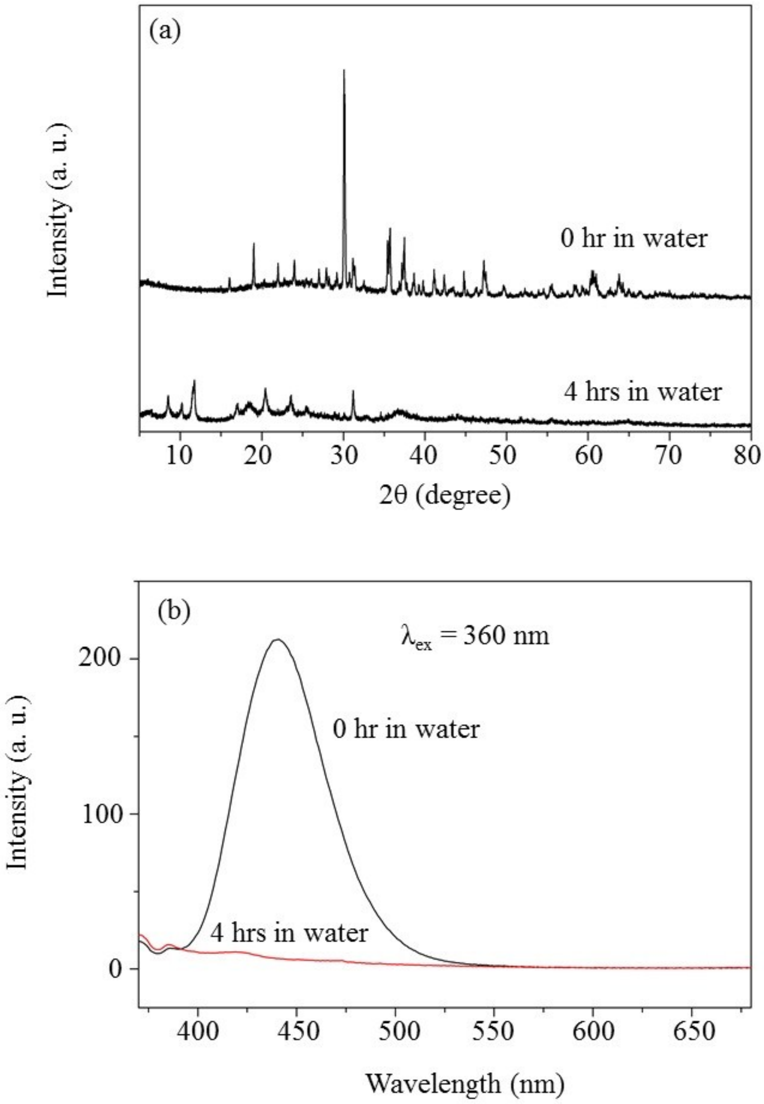

Figure S3. (a) XRD patterns and (b) emission spectra of the commercial Al-based violet-emitting LLP before and after immersion in water for 4 hours.

2. Morphology

In order to further demonstrate the loaded structure of Ag/AgCl on the surface of $Ca_2Al_2SiO_7$: Ce^{3+} LLPs, SEM images together with EDS spectra of G and G10A1 are compared in Figure S4. The bare gehnelite image looks like the aggregates of smaller particles (Figure S4 (a)). Only the element of Ca, Al, Si and O are detected from their surfaces. On contrary, grape-like small aggregates of Ag/AgCl nanoparticles are decorated on the surface of gehnelite particles (Figure S4 (c, e)), exhibiting a rougher surface as compared to the smoother one of the bare gehnelite (Figure S4 (a)). The existence of Ag and Cl on the surface was confirmed by the EDX analysis (Figure S4 (d)). While the method and conditions used for preparing Ag/AgCl particles in the current work tend to give the photocatalyst with smaller particle sizes (refer to the Materials Synthesis and Results and Discussion section), we do observe some bigger nanoparticles with cubic (AgCl) morphology (Figure S4 (f)) beside the smaller nanoparticles.

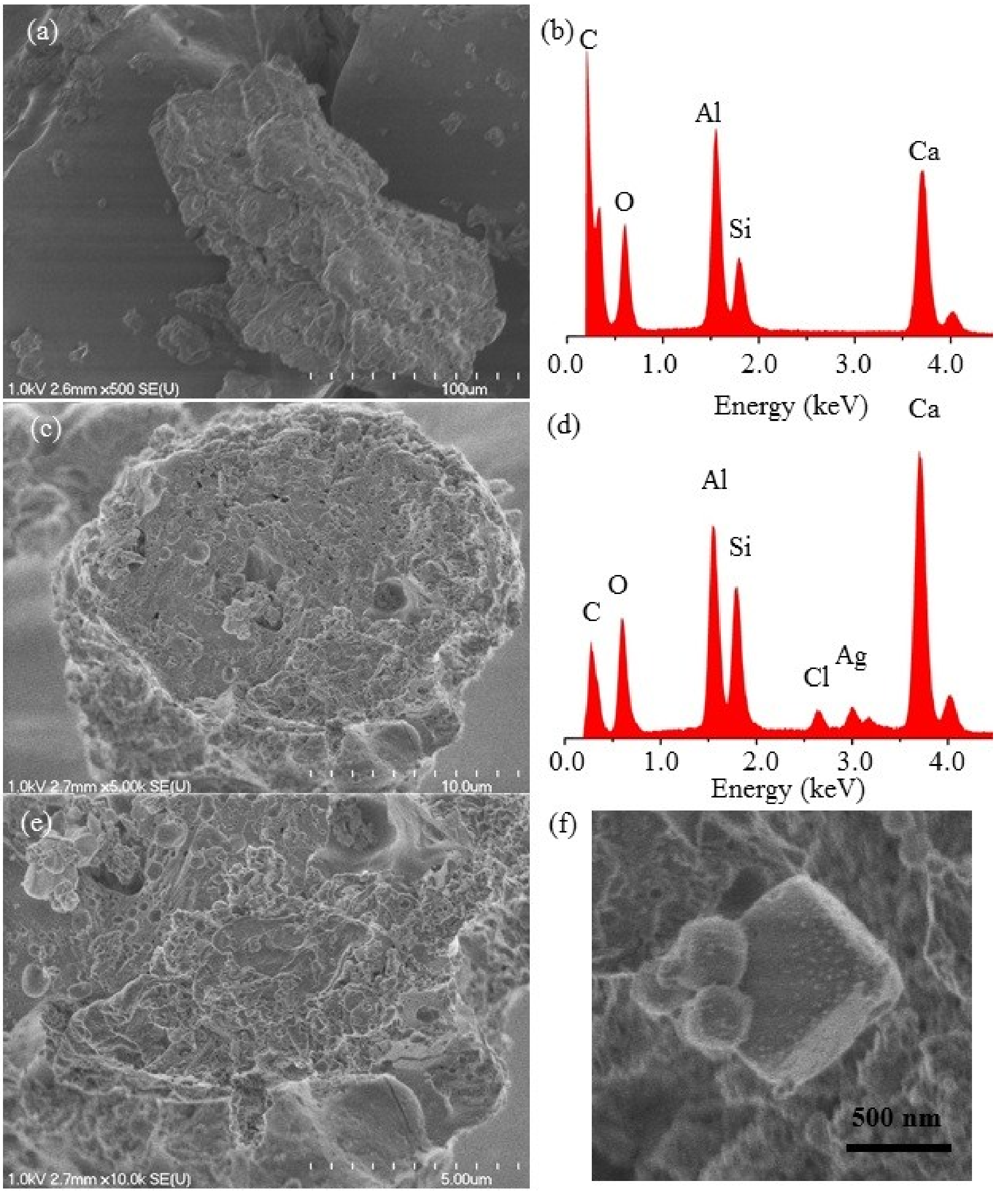

Figure S4. SEM images and EDX spectra of G (a, b) and G10A1 (c-f).

3. Recyclability test

Three repeating runs of MO degradation experiments with the same G10A1 sample, which was collected, washed sufficiently by distilled water, and dried after the use of the previous run, were performed. As shown in Figure S5, the results demonstrate a very good reproducibility for the photocatalytic activity under solar irradiation, but that in the long-lasting part gradually decreased. With increasing repeating numbers, the color of the catalyst was found to become darker, indicating that solar irradiation results in the gradual reduction of Ag^+ to Ag^0. This is evidenced by the enhanced absorption in the wavelength range of > 284 nm by the used photocatalyst as shown by the UV-vis spectrum in Figure S6. As the enhanced absorption range of the used catalyst overlaps with the absorption band of G, we consider that the increased irradiation filtering effect on LLPs due to the reduced active species (Ag/AgCl) is responsible for the gradual decrease of photoactivity in the long-lasting part.

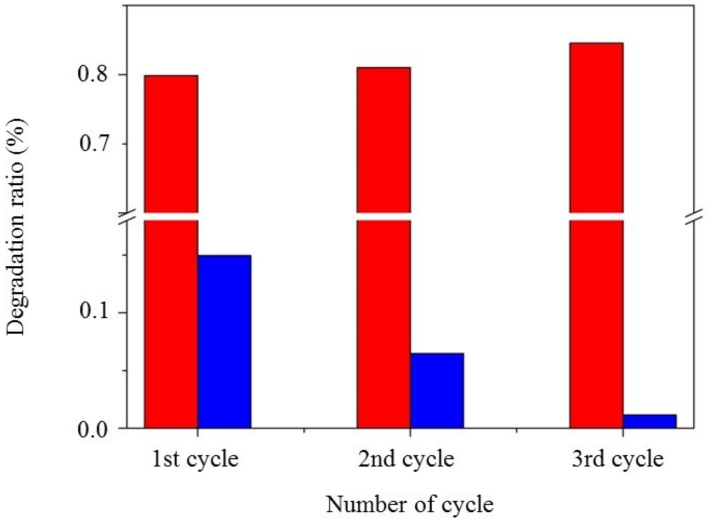

Figure S5. MO degradation ratio of G10A1 in three runs. The degradation ratios are defined as C/C_0 and C/C_{A0}, respectively, for those under irradiation (red bar) and the long-lasting part (blue bar)

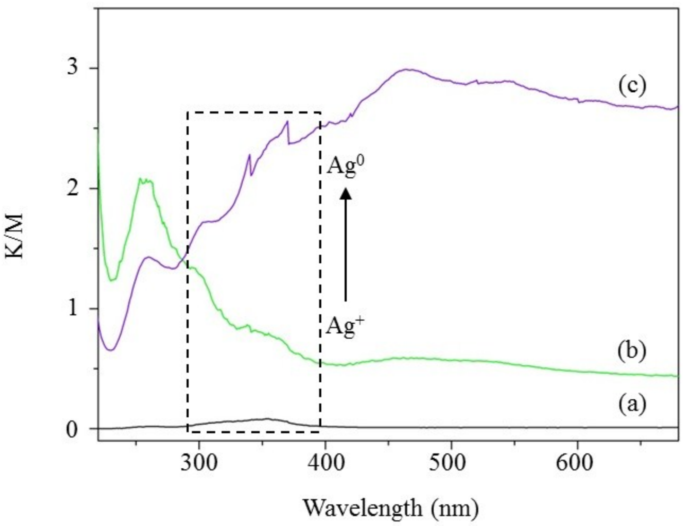

Figure S6. DRS spectra of G (blue), the fresh G10A1 (red) and the G10A1 used after three cycle photocatalytic experiment (green).