A novel preparation method for ZnO/γ-Al₂O₃ nanofibers with enhanced absorbability and improved photocatalytic water-treatment performance by Ag nanoparticles

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0.4 g ZnAc$_2$ $\cdot$2H$_2$O was mixed with 0.1 g, 0.2 g and 0.3 g AlCl$_3$ during the synthesis, and the prepared ZnO/$\gamma$-Al$_2$O$_3$ nanofibers were named as AZ1, AZ2 and AZ3, respectively. The XRD patterns of ZnO and ZnO/$\gamma$-Al$_2$O$_3$ nanofibers with different aluminum ratio were characterized. It can be seen from Fig. S1 that the peak of $\gamma$-Al$_2$O$_3$ increased with aluminum composition.

Figure S1. The XRD patterns of the as-synthesized ZnO/$\gamma$-Al$_2$O$_3$ nanofibers with different aluminum composition.
The ZnO/γ-Al₂O₃ nanofibers with different aluminum ratios were compared to further characterize the adsorption and photocatalytic performance, and the results are shown in Figure S2. Adsorption degradation (in dark) and photocatalytic degradation of MO (under UV illumination) by various nanofibers were done under the same condition as described in Fig. 6. The ZnO/γ-Al₂O₃ with the mass ratio of ZnAc₂ •2H₂O : AlCl₃ = 2:1 during the synthesis procedure (AZ2) exhibited the best catalytic activity.

Figure S2. Adsorption degradation (A) and photocatalytic degradation (B) of MO using the as-prepared samples (ZnO, AZ1, AZ2, AZ3).
To understand the chemical composition of the obtained samples, EDS analysis was performed on the ZnO, ZnO/γ-Al₂O₃ (AZ2), photoreduced-Ag/ZnO/γ-Al₂O₃ and hydrothermal-Ag/ZnO/γ-Al₂O₃ nanofibers. The peaks and the elemental mapping of photoreduced-Ag/ZnO/γ-Al₂O₃ nanofibers can be clearly observed in Figure S3E-G.

Figure S3. The EDS results of (A) ZnO, (B) ZnO/γ-Al₂O₃ (AZ2), (C) photoreduced-Ag/ZnO/γ-Al₂O₃, and (D) hydrothermal-Ag/ZnO/γ-Al₂O₃. (E) SEM of photoreduced-Ag/ZnO/γ-Al₂O₃ nanofibers, EDS mapping for (F) Zn and (G) Ag elements in the photoreduced-Ag/ZnO/γ-Al₂O₃ nanofibers.
As a comparison material, pure ZnO nanofibers were synthesized using the same method as that of the ZnO/γ-Al₂O₃. The SEM and TEM images in Figure S4 confirm that the pure ZnO nanofibers have mono-crystal and non-porous structures.

Figure S4. SEM (A) and TEM images (B) of the as-prepared ZnO nanofibers.
Adsorption mechanism study using Brunauer–Emmett–Teller (BET) theory

The $\text{N}_2$ adsorption/desorption was employed to study the surface properties of the ZnO/$\gamma$-Al$_2$O$_3$ nanofibers. The isotherm of the AZ2 fibers exhibits a type-III curve in Figure S4, which is a typical characteristic of mesoporous and macro-porous materials. The synthesized AZ2 has a surface area of 25.4 m$^2$/g according to the BET theory. Therefore, we speculate that the excellent adsorption effect should not be a result of this small surface area.

Figure S5. The determination of the surface area of ZnO/$\gamma$-Al$_2$O$_3$ nanofibers using BET theory.
FTIR Analysis

FTIR spectroscopy was introduced to characterize the samples before and after MO adsorption for a better understanding of the adsorption mechanism, and the results are plotted in Figure S5. The FTIR spectrum of the ZnO/γ-Al₂O₃ nanofibers (AZ2) shows obvious S=O stretching vibrations at 1122 cm⁻¹ and 1194 cm⁻¹ after the MO adsorption. This means that the adsorption process was not depended on the surface functional group such as hydroxyl or carboxyl. According to hard-soft acid-base (HSAB) theory, we claim that the main mechanism of the MO adsorption process is the interaction with aluminum ion by the way of coordination.

Figure S6. The FTIR spectra of ZnO/γ-Al₂O₃ before and after the MO adsorption.
Figure S7. The UV-vis absorption spectra recorded for the adsorption properties and photocatalytic performance of the MO degraded by photoreduced-Ag/ZnO/γ-Al$_2$O$_3$ nanofibers.