Electronic Supplementary Material (ESI) for Environmental Science: Nano. This journal is © The Royal Society of Chemistry 2018

Electronic supplementary information for: 1 2 Impacts of Titanium Dioxide Nanoparticles on Transformation of Silver **Nanoparticles in Aquatic Environments** 3 4 Yinqing Zhang,^{‡a} Liwen Qiang,^{‡b} Yuting Yuan,^a Wei Wu,^a Binbin Sun^a and Lingyan Zhu^{*a} 5 6 7 ^a Key Laboratory of Pollution Processes and Environmental Criteria (Ministry of Education), Tianjin 8 Key Laboratory of Environmental Remediation and Pollution Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300350, P. R. China 9 ^b Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin 300191, P. R. China 10 [‡] These authors contributed equally to this article. 11 12 13 14 15 16 17 18 Summary 19 20 Number of Pages: 17 Page S2-S17: Fig. S1-Fig. S16 21 22



 $24 \quad Fig. \ S1 \ The \ variation \ of \ Ag^+ \ concentration \ in \ the \ absence \ of \ nano-TiO_2 \ under \ sunlight \ irradiation. \ The \ absence \ of \ nano-TiO_2 \ under \ sunlight \ irradiation.$

25 $\,$ initial concentration of Ag^+ ions was in the range from 20 to 500 $\mu g/L$ and the concentration of nano-

 $26 \quad TiO_2 \ was \ 200 \ \mu g/L. \ The \ depletion \ of \ Ag^+ \ ions \ was \ marginal, \ and \ could \ be \ negligible \ in \ the \ calculation$

27 of photoreduction rate constant in the presence of nano-TiO₂.



29 Fig. S2 UV-vis absorption spectra of nano-TiO₂ suspensions (1 mg /L) in dark and under simulated

30 sunlight irradiation for 12 h. No absorption peak was detected in the wavelength range of 300-700 nm,

31 suggesting that nano-TiO₂ did not affect the spectra of AgNPs.



33 Fig. S3 TEM image of the synthesized AgNPs. The scale bar of the image represents 50 nm.



35 Fig. S4 TEM image of the nano-TiO₂ used in this study. The scale bar of the image represents 20 nm.



Fig. S5 UV-vis absorption spectra of the experiment solution with different initial concentrations of Ag⁺ ions in the presence of 200 μ g/L nano-TiO₂. (a) 50 μ g/L Ag⁺ ions in dark. (b) 200 μ g/L Ag⁺ ions in dark. (c) 500 μ g/L Ag⁺ ions in dark. (d) 50 μ g/L Ag⁺ ions after 10 min of sunlight irradiation. (e) 200 μ g/L Ag⁺ ions after 10 min of sunlight irradiation. (f) 500 μ g/L Ag⁺ ions after 10 min of sunlight irradiation.



43 Fig. S6 Log-linear relationship between the concentration of silver ions and reaction time from Fig.
44 1B at different initial Ag⁺ ion concentration at the early stage of the reaction (0-1 h). The overall R²
45 value is 0.91.



47 Fig. 7 TEM image of the solid particles in the binary solution of nano-TiO₂ and AgNPs in dark for 12
48 h. The scale bar of the image represented 100 nm.



50 Fig. S8 Aggregation profile obtained from single and binary suspensions of AgNPs and nano-TiO₂

51 with different initial concentrations.



Fig. S9 The concentration of dissolved Ag⁺ ions in the solutions in dark with different concentrations of nano-TiO₂. The initial concentration of AgNPs was 200 μ g/L. Data points represented the average of three independent replicates.



56

Fig. S10 The concentration of dissolved Ag^+ ions in the solutions under simulated sunlight irradiation with different concentrations of nano-TiO₂. The initial concentration of AgNPs was 200 µg/L. Data points represented the average of three independent replicates.





61 Fig. S11 X-ray photoelectron spectra of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ from the product in the reaction 62 suspension under sunlight irradiation. The initial concentration of AgNPs and nano-TiO₂ was 200 µg/L 63 and 1 mg/L, respectively.



65 Fig. S12 Log-linear relationship between $I(AgNPs) / I_0(AgNPs)$ and reaction time from Fig. 6 with 66 different initial concentrations of nano-TiO₂.



Fig. S13 UV-vis absorption spectra of AgNPs solutions in the presence of FA (1 mg C/L) under dark
condition over different experiment duration. (A) Blank experiment, in the absence of nano-TiO₂. (B)
Initial concentration of nano-TiO₂ was 50 μg/L. (C) Initial concentration of nano-TiO₂ was 200 μg/L.
(D) Initial concentration of nano-TiO₂ was 1 mg/L.



72

Fig. S14 UV-vis absorption spectra of AgNPs solutions in the presence of FA (1 mg C/L) under simulated sunlight irradiation over different experiment duration. (A) Blank experiment, in the absence of nano-TiO₂. (B) Initial concentration of nano-TiO₂ was 50 μ g/L. (C) Initial concentration of nano-TiO₂ was 200 μ g/L. (D) Initial concentration of nano-TiO₂ was 1 mg/L.



77

Fig. S15 The concentration of dissolved Ag^+ ions in the solutions under sunlight irradiation in the presence of FA with different concentrations of nano-TiO₂. The initial concentration of AgNPs was 200 μ g/L. Data points represented the average of three independent replicates.



81

Fig. S16 DMPO spin-trapping ESR spectra recorded in the absence and presence of FA under simulated sunlight irradiation. The sample suspensions contained 200 μ g/L AgNPs and 200 μ g/L nano-TiO₂.