Supporting Information

The detailed study of the photodegradation process of Orange G.

UV/Vis, TOC and GC/MS Analysis

To monitor the progress of photodegradation of Orange G and the decolorization of the solution, UV/Vis spectra were recorded between 200 and 660 nm employing a TU-1810 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd) equipped with 10 mm quartz cuvettes. The degradation of Orange G and the decolorization of the solution were followed by determining the concentration of the remaining dye in the solution.

The degree of mineralization of the dye was evaluated by the total organic carbon (TOC) removal. TOC of the solution was analysed by an Apollo 9000 TOC Analyzer (Tekmar-Dohrmann) with Non-Dispersive Infra-Red (NDIR) detector.

Some organic intermediates have been analyzed employing a gas chromatography–mass spectrometry (6890/5793N GC–MS, Agilent Corporation, USA). A HP-5 (Hewlett Packard, USA, 30 m × 0.25 mm × 0.25 μm) capillary column has been used for this intermediate determination at the following conditions: column temperature programmed from 80 °C for 6 min, ramp first at 200 °C with a 20 °C/min rate, then raised to 280 °C at a rate of 10 °C/min; carrier gas, helium, flow rate 1.8 mL/min; T_injector = 250 °C; T_detector = 280 °C; volume injected 2 μL; ionization energy 70 eV, mass scan range 30–380 amu. Identification of the GC/MS spectral features was achieved with the use of a build-in library.

The samples for GC-MS analysis were prepared as follows: at the given time of 10 min, the analytical samples were taken from the suspension and immediately centrifuged at 40 rps for 15 min, then filtered through a 0.45 μm Millipore filter to remove the particles. The filtrate (50 mL) was acidified (pH < 2) and extracted with dichloromethane (10 × 20 mL). The extracts were dried on anhydrous sodium sulfate overnight. The finished sample was esterified using concentrated H_2SO_4 and absolute
ethanol and then concentrated to 1mL under reduced pressure for GC/MS analysis. Utilization of this method allowed for identification of some important reaction intermediates shown in Table S1.

Results and Discussion

It is found that the absorbance spectrum of Orange G in water is characterized by two bands in the visible region (with their maxima located at 472 and ca. 420 nm), and the other two bands in the ultraviolet region (with their maxima located at 248 and 331 nm). The absorbance peaks at 248 and 331 nm are due to the benzene and naphthalene rings of Orange G, respectively. The two bands in the visible region are due to the chromophore-containing azo linkage and are attributed to the presence of two forms of the dye molecules in solution, as shown by scheme S1.

Orange G is subjected to intramolecular hydrogen bonding tautomeric interactions between the oxygen of the naphthyl group and the β-hydrogen of the corresponding azo linkage (Scheme S1). The band at 472 nm corresponds to the hydrazone form, while the shoulder at 420 nm is linked to the azo form of the dye. The ratio of the hydrazone form to the azo form is much higher in water than in organic solvents, as the hydrazone form is favored by water and the azo form by polar organic solvents. Therefore, this tautomerism of the aqueous solution of Orange G favors the hydrazone form and the main absorption band at 472 nm is linked to that form of Orange G. So, the concentration of the remaining Orange G in the photocatalytic process was
calibrated based on the Beer-Lambert law at its maximum absorption wavelength 472 nm.

**Figure S1.** TOC values vs. irradiation time (initial dye concentration = 10 ppm, amount of 1.6 at.% Ag/ZnO = 100 mg).

**Figure S2.** The remaining percents of TOC and dye versus the irradiation time.
As seen from the curves in Figure 6 in the text, the reduction in the absorbance peaks at 248, 331 and 472 nm indicated the degradation of the dye molecules into smaller intermediates. However, it has been reported that some major transient intermediates are more harmful than the original dyes. Therefore, reduction of the TOC content of the solution at interval time was also evaluated in order to verify whether the Orange G and the intermediates are mineralized. The results were shown in Figure S1. It can be seen that, about 60 min is required for complete degradation of Orange G under the given experimental conditions. For the purpose of comparison, Figure S2 shows the percentage of TOC and Orange G color remaining. It can be clearly seen that the percents of decolourisation and degradation increase with increase of irradiation time. However, the rates of decolourisation and mineralization are not the same (i.e., the removal of the dye colour and the TOC are not synchronous), and the photodegradation proceeds with a slow kinetics after 20 min irradiation. This indicates the formation of intermediates and their competition with parent Orange G molecules in the photocatalytic process. So, under the given experimental conditions the complete decolourisation of Orange G occurs in 50 min., while 60 min is required for its complete mineralization.

Some important reaction intermediates were analysed by GC/MS spectroscopy and the results are show in Table S1

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**Table S1.** Some important reaction intermediates identified by GC/MS spectroscopy.