Electronic Supplementary Information (ESI)

Efficient visible light photocatalytic degradation of 17α-ethinyl estradiol by multifunctional Ag-AgCl/ZnFe$_2$O$_4$ magnetic nanocomposite

Akhanda Raj Upreti [a], Yi Li*[a], Nirina Khadgi [a], Saraschandra Naraginti [a] and Chi Zhang [a]

[a] *Key Laboratory of Integrated Regulation and Resource Development of Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Xikang Road #1, Nanjing 210098, P.R. China.*

 ***Corresponding Author. Tel: +86 013776417768; *E-mail address*: envly@hhu.edu.cn
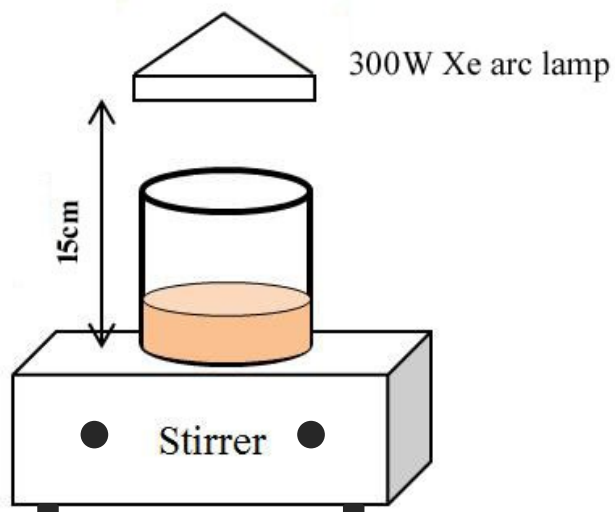
Experimental Setup

Figure S1. Experimental setup for photocatalytic degradation
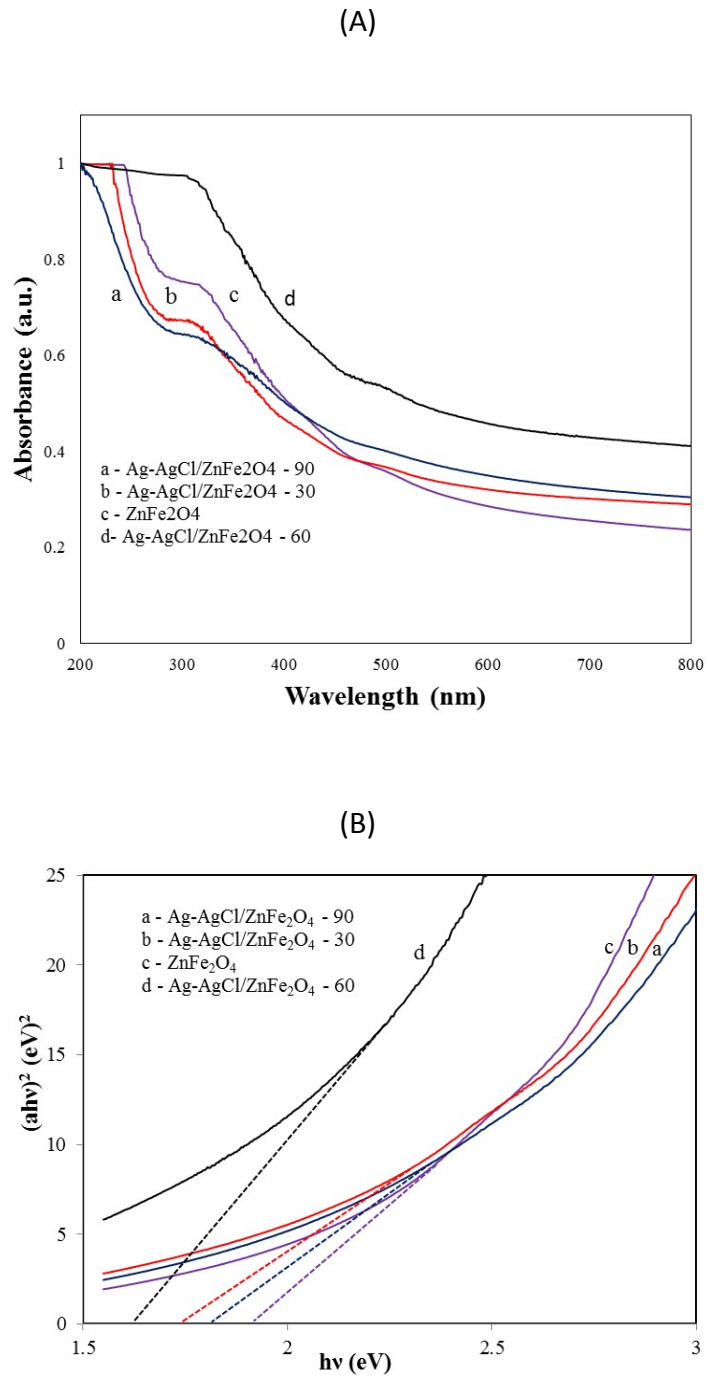
UV-Vis DRS absorbance spectra

(A)

(B)

Figure S2. (A) Normalised UV-Vis spectrum of the composites (B) Plots of (αhν) ^{2} versus photo energy (hν) for various NCs
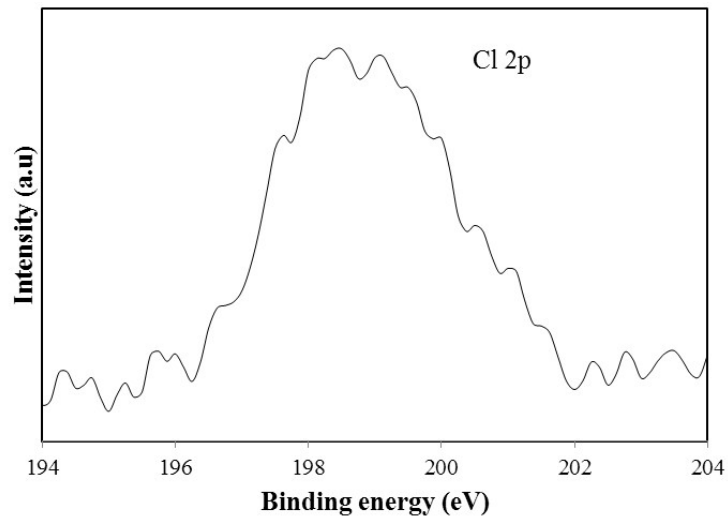
Figure S3. XPS of Cl 2p binding energy

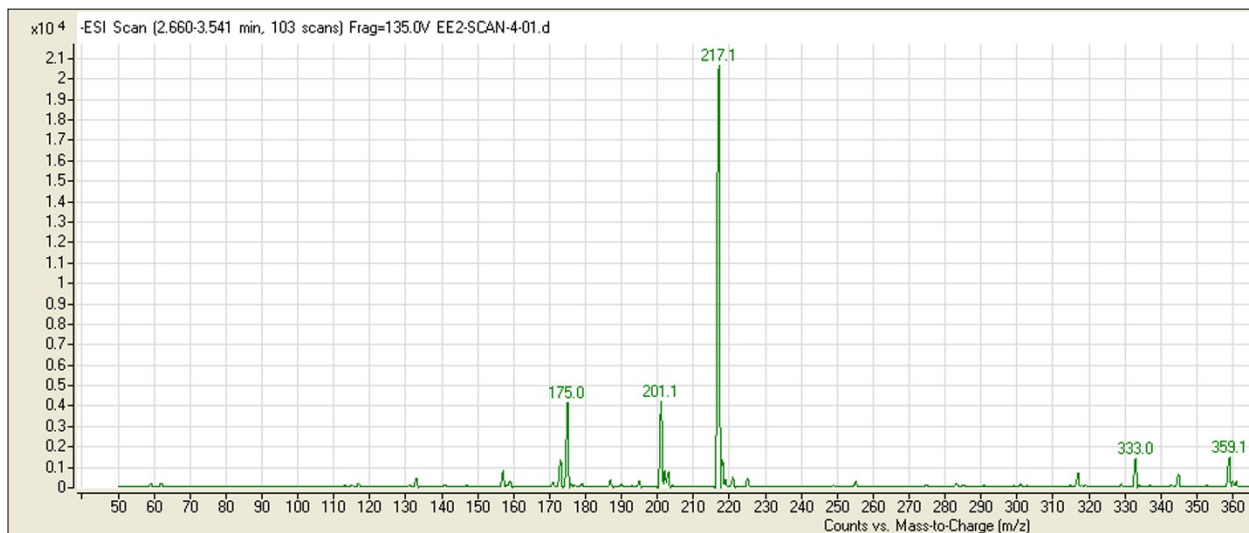## LC-MS study of EE2: Mass Fragmentation patterns

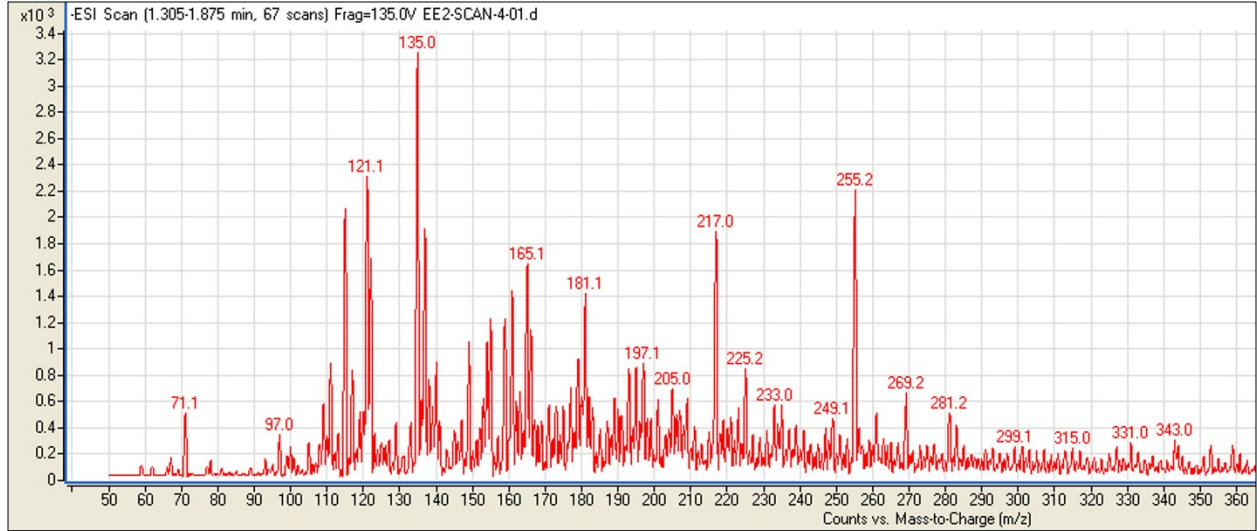**Figure S4.** Mass fragmentation pattern of EE2 at 120 minutes

Figure S5. Mass fragmentation pattern of EE2 at 240 minutes

Calculation of TON and TOF.

TON and TOF were calculated based on the method given by Umar et al. 2014. Briefly, for the determination of the turnorver number (TON) and turnover frequency (TOF) of Ag-AgCl/ZnFe$_2$O$_4$ nanocomposite (NC) in the photocatalytic degradation of EE2, we firstly calculated the active sites (AS) number (i.e. the effective site on Ag-AgCl/ZnFe$_2$O$_4$ nanocomposite surface for EE2 adsorption and heterogeneous catalytic reaction). For heterogeneous catalysis it is possible to set the rate as a function of the surface area ("TOFarea") (Kozuch and Martin, 2012). Therefore, here, we estimated the active site using the obtained BET surface area. Nitrogen adsorption–desorption isotherm measurements were performed on a Quantachrome Autosorb 1 instrument to study specific surface area and found out to be 20.1 m^{2}g^{-1}.

The amount of EE2 molecules accommodated on the catalyst surface was assumed to reflect the number of active site on the catalyst surface. The molecular diameter of EE2 is 0.6 nm (i.e. 6 × 10^{-10} m) (Li et. al, 2013). The cross-section of single EE2 molecule was considered equivalent to the area on the catalyst surface occupied by the EE2. Thus,

$$EE2_{CS} = 3.14 \times \left(\frac{D}{2}\right)^2 = 3.14 \times \left(\frac{6 \times 10^{-10}\,m}{2}\right)^2 = 2.826 \times 10^{-19}\,m^2 \text{ ... (1)}$$

Where D = EE2 molecular diameter

BET surface area (**BET_{SA}**) = 20.1 m^2 g^{-1}.

Amount of catalyst used was 50 mg in 100 mL of EE2 solution; i.e. 0.05 g

The BET surface areas reflect the number of adsorption sites and not necessarily the number of catalytically active sites. On this point, we assumed that about 10% or less of the surface sites may be active in any given catalytic reaction/process, and that the specific TON is only a conservative estimate of the real turnover (Somorjai, 1989).

Hence, the specific surface area (**SSA**) of Ag-AgCl/ZnFe$_2$O$_4$ NC become:

$$SSA = BET_{SA} \times MG = 10\% \, of \, 20.1 m^2 g^{-1} \times 0.05g = 0.1005 m^2$$

The number of active sites (**AS**) on the catalyst surface was calculated by dividing the specific surface area (**SSA**) with the EE2 cross-section (**EE2$_{CS}$**).

$$AS = \frac{SSA}{EE2_{CS}} \, ... \, (2)$$

For the calculation of the TON and TOF of the Ag-AgCl/ZnFe$_2$O$_4$ NC in the degradation of EE2 molecules the number of EE2 molecules degraded was divided by the number of active sites (**AS**).

From the experimental data, at 30 minutes on reaction, 51.5% of EE2 molecules have been degraded. Since the initial concentration of EE2 is 5 ppm (100 mL), the **EE2$_{deg}$** is:

$$EE2_{deg} = x\% \times N_{init} \, ... \, (3)$$

Where **N$_{init}$** = initial number of EE2 molecules= $\dfrac{5 \times 10^{-4} g}{296.178 g / mol} \times 6 \times 10^{23} \, molecules / mol$

i.e., $EE2_{deg} = 51.5\% \times \dfrac{5 \times 10^{-4} g}{296.178 g / mol} \times 6 \times 10^{23} \, molecules / mol$

The TON was calculated by dividing (3) by (2), and the TOF was obtained by dividing TON with reaction time.

Table S1. TON and TOF values at different time of photocatalytic degradation of EE2

Time	%EE2 degraded	TON	TOF (min^{-1})
120	88.3691	25.1695	0.209745911
90	81.5618	23.2307	0.258118441
60	68.8633	19.6138	0.326897319
30	51.4717	14.6603	0.488677374
20	35.4037	10.0838	0.504189389

The estimates of turnover numbers in our study represent the lower limits only and do not correspond to the actual TON values. However, even these lower limits tell us that the photoprocesses in this study are photocatalytic rather than stoichiometric.

References:

A. A. Umar, E. Rahmi, A. Balouch, M. Y. A. Rahman, M. M. Salleh and M. Oyama, *J. Mater. Chem. A*, 2014, **2**, 17655

A. V. Emeline, A. V. Panasuk, N. Sheremetyeva, and N. Serpone., *J. Phys. Chem. B* **2005,** *109,* 2785-2792.

G. Somorjai, in: N. Serpone, E. Pelizzetti (Eds.), Photocatalysis — Fundamentals and Applications, Wiley/Interscience, New York, 1989 (Chapter 9).

J. Li, L. Jiang, X. Xiang, S. Xu, R. Wen, and X. Liu, *Journal of Environmental Sciences (China),* 2013., 25, **6**, 154–1163.

S. Kozuch and J. M. L. Martin. *ACS Catal.* 2012, **2**, 2787–2794.