

Supplementary data

**Rapid dehalogenation of pesticides and organics at the interface of reduced
graphene oxide-silver nanocomposite**

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Supplementary data S1

About 25 mL concentrated H_2SO_4 , 5 g of $\text{K}_2\text{S}_2\text{O}_8$ and 5 g of P_2O_5 were taken in a 250 mL beaker and were heated at $90\text{ }^\circ\text{C}$ with constant stirring. When all these reactants got completely dissolved, the temperature of the reaction was then decreased to $80\text{ }^\circ\text{C}$. Then 6 g of graphite powder was added slowly to this reaction mixture. Initially, bubbling was observed. It subsided subsequently, over a period of about 30 min. After that the temperature of the reaction mixture was maintained at $80\text{ }^\circ\text{C}$ for 5 h. The reaction was stopped and cooled at room temperature. The mixture was then diluted with 1 L of distilled water and then left undisturbed overnight. The resultant solution was then filtered and washed to remove excess acid present and the solid product was dried overnight in air.

This pre-oxidized graphite obtained was then added to 230 mL of concentrated H_2SO_4 which was already being maintained at $0\text{-}5\text{ }^\circ\text{C}$ in an ice bath. It was followed by stirring. 15 g of KMnO_4 was added slowly such that the temperature does not go beyond $10\text{ }^\circ\text{C}$. The temperature was then raised to $35\text{ }^\circ\text{C}$. The reaction was then allowed to undergo for another 2 h. Subsequently, 1 L of distilled water was added carefully keeping into consideration that the temperature should not go above $50\text{ }^\circ\text{C}$. The reaction mixture was again stirred for two more hours. 1.5 L of distilled water and 25 mL of 30% H_2O_2 were added to it. Then the mixture was kept at room temperature for a day. After that the supernatant was decanted and the remaining solution was centrifuged and washed with 10% HCl which was followed by distilled water. This process was repeated a number of times. The resultant solid was dried and then 2 wt% (w/v) dispersion was prepared in distilled water. This dispersion was dialyzed for 3 weeks in order to remove all the unwanted contaminants like salts and acid. Finally the dispersion was diluted to obtain 0.5 wt% (w/v) graphene oxide (GO).

Now to obtain reduced graphene oxide (RGO), pre reduction of GO was carried by adding Na_2CO_3 (5 wt%) and 800 mg NaBH_4 followed by heating for 1 h. The reaction mixture was cooled, centrifuged and rinsed with water several times and then re-dispersed in water. Now to increase the stability of graphene in water, a simple sulfonation procedure was followed by introducing sulfonic acid groups in RGO. 20 mg sulfanilic acid and 8 mg sodium nitrite were first dissolved in 0.25% NaOH solution. Then 4 mL, 0.1 M HCl was added to it. The reaction mixture was kept in an ice bath under stirring. After 15 min, the aryl diazonium salt solution was added to 20 mL, 0.5 mg/mL RGO dispersion. This reaction was also carried in an ice bath with continuous stirring for 2 h. After 2 h, the solution was filtered, washed and re-dispersed in distilled water. The final concentration of 0.05 wt% RGO was obtained with solution pH value 6.

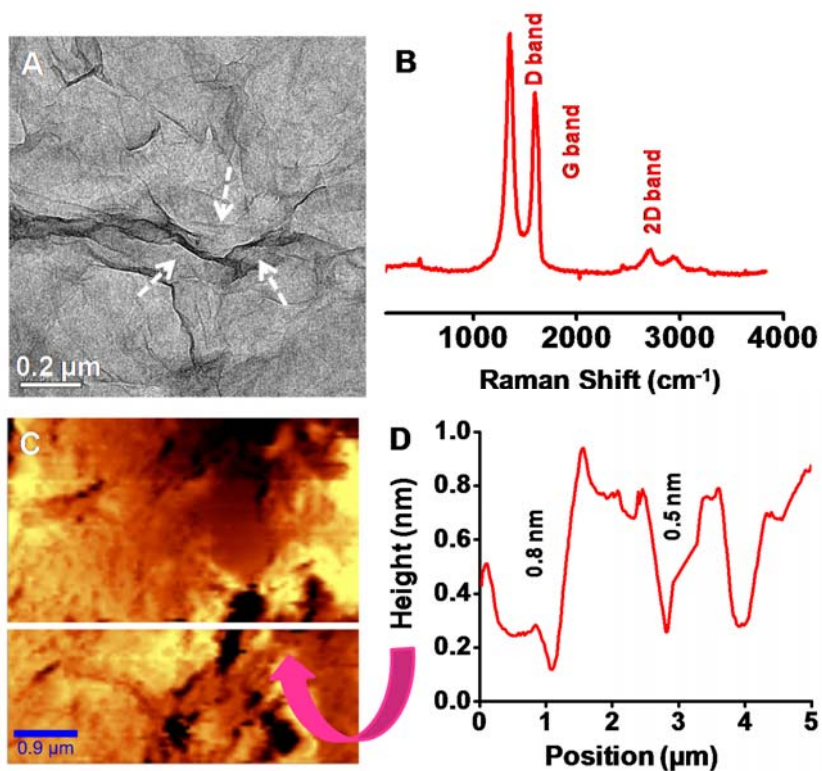


Fig. S1: A) TEM image of graphene showing the foldings marked in white arrows. B) Raman spectrum showing the presence of D, G and 2D bands. C) AFM image and D) Height profile (taken along the white line of image (C)) showing 2-3 layered RGO.

Supplementary data S2

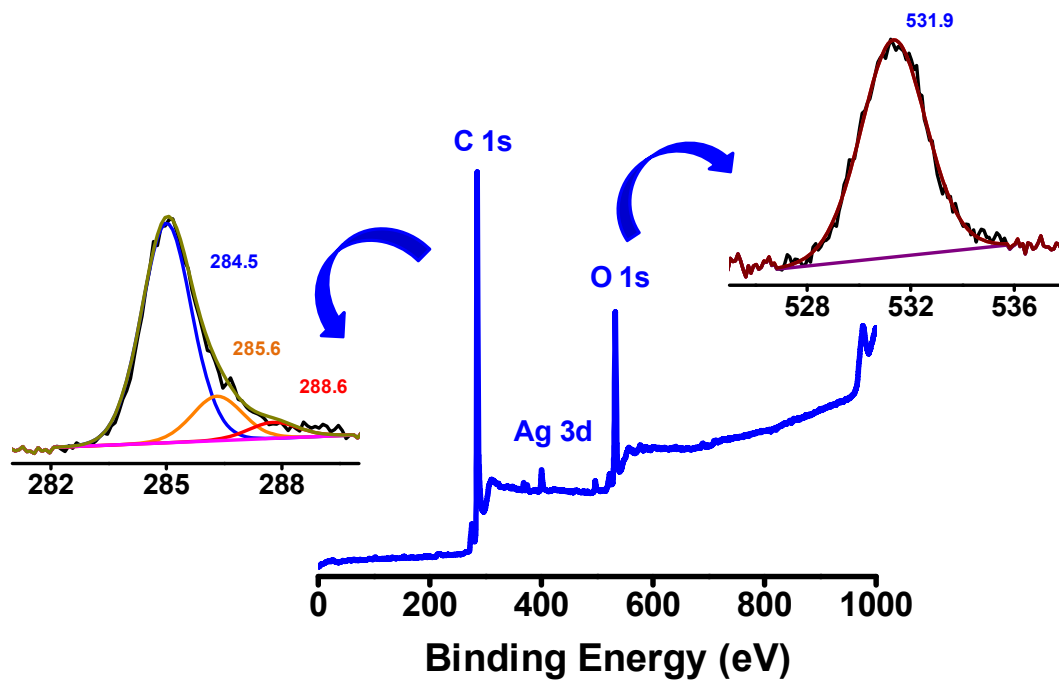


Fig. S2: XPS survey spectrum of RGO@Ag showing the presence of carbon, oxygen and silver.

The deconvoluted spectrum of C 1s and O 1s are represented with a marked arrow.

Supplementary data S3

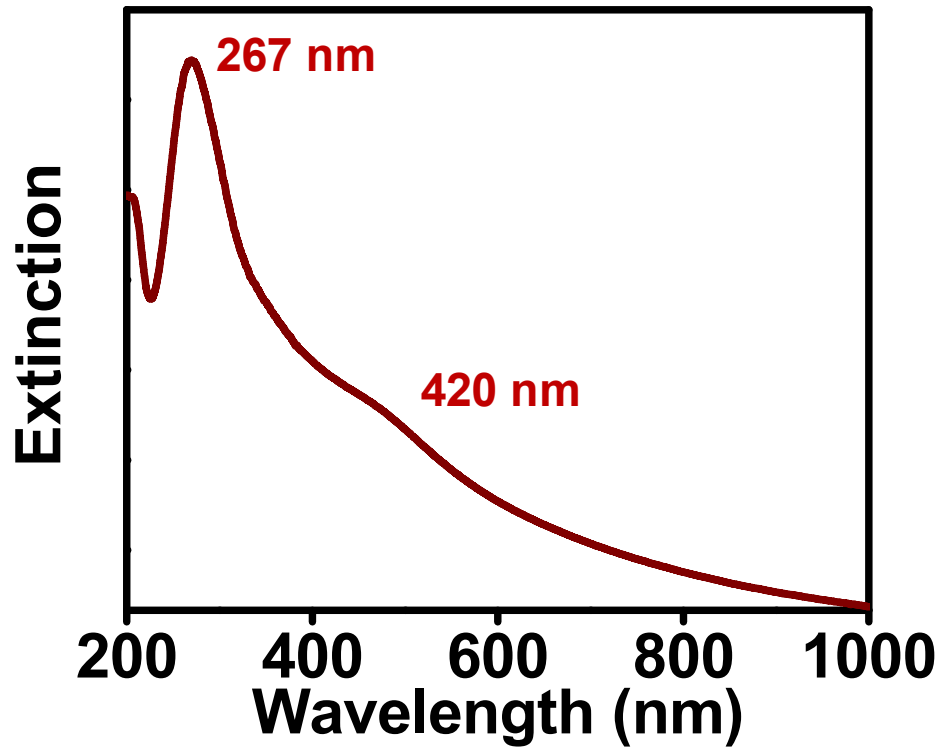


Fig. S3: UV/vis spectrum of RGO@Ag. The peak at 267 nm is characteristic of RGO and the other peak at around 420 nm is due to the plasmon resonance of Ag NPs.

Supplementary data S4

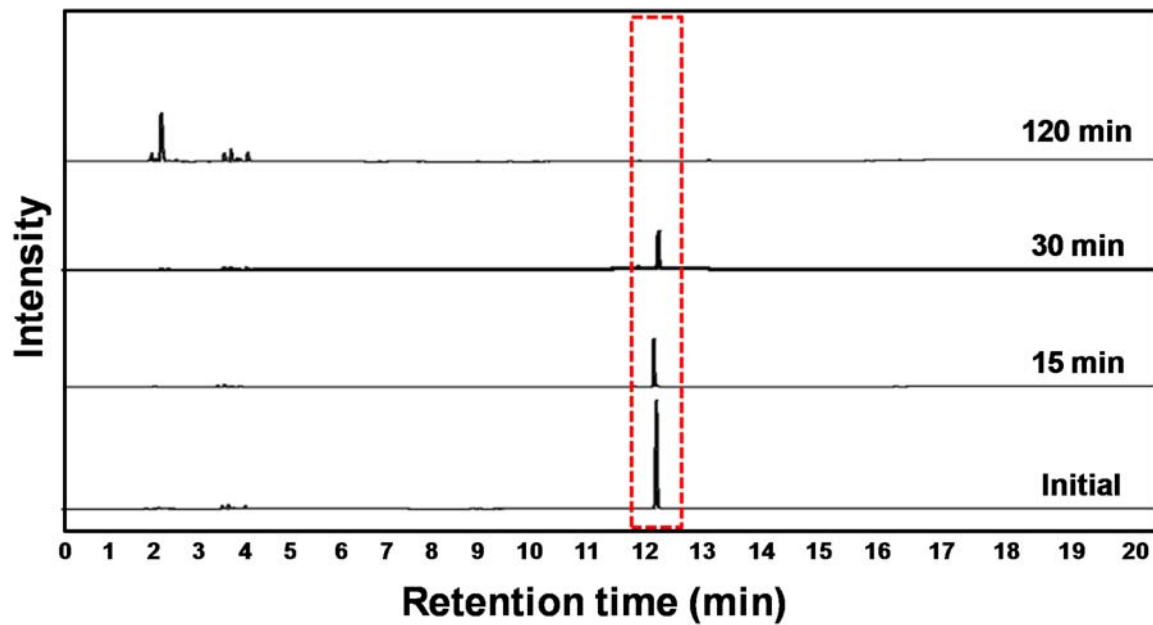


Fig. S4: Time dependent GC-ECD showing complete removal of pesticide CP from water with respect to time when reacted with RGO@Ag composite. The CP region is highlighted.

Supplementary data S5

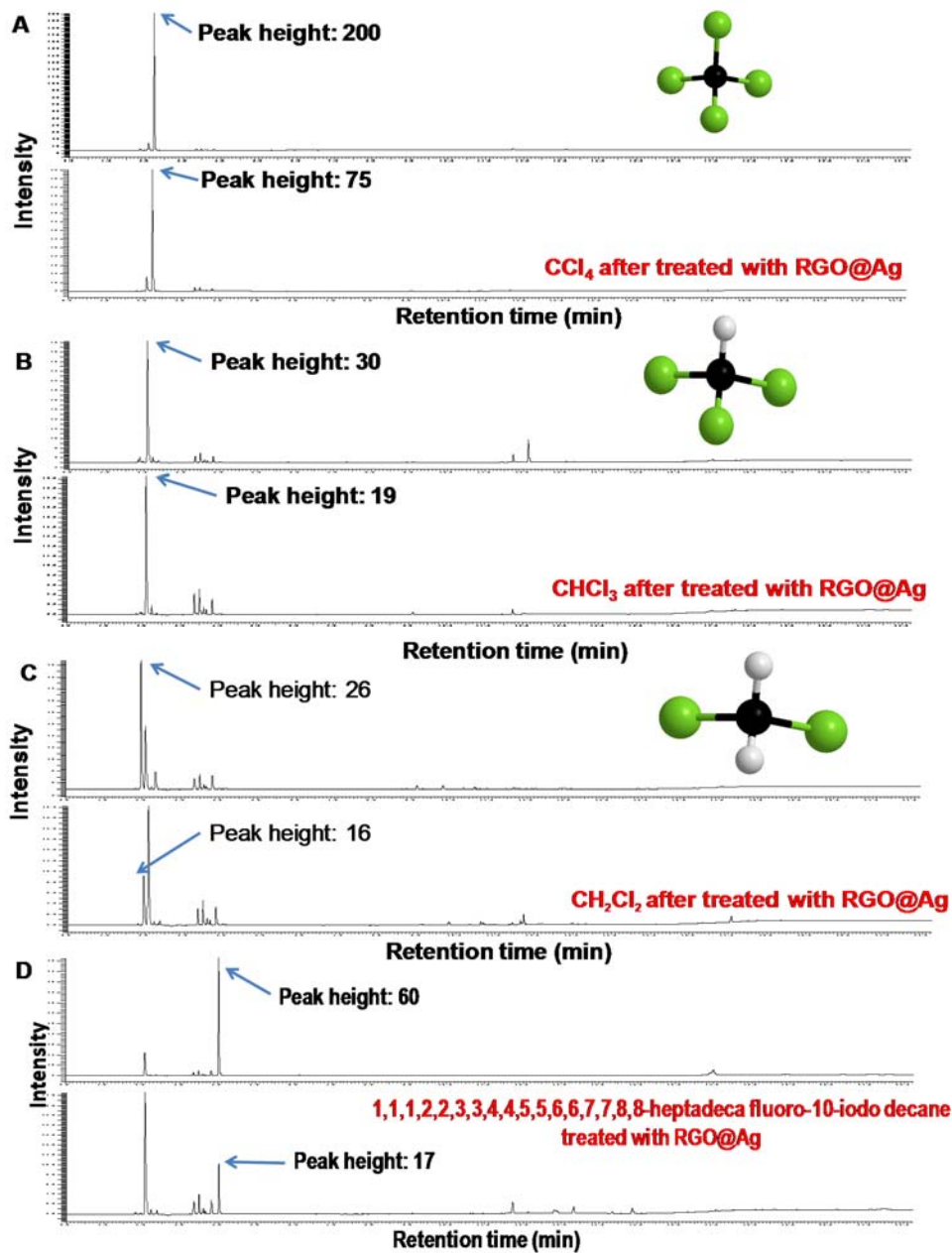


Fig. S5: GC-ECD showing the removal of A) CCl₄, B) CHCl₃, C) CH₂Cl₂ and D) HFID after the reaction with RGO@Ag composite.

Supplementary data S6

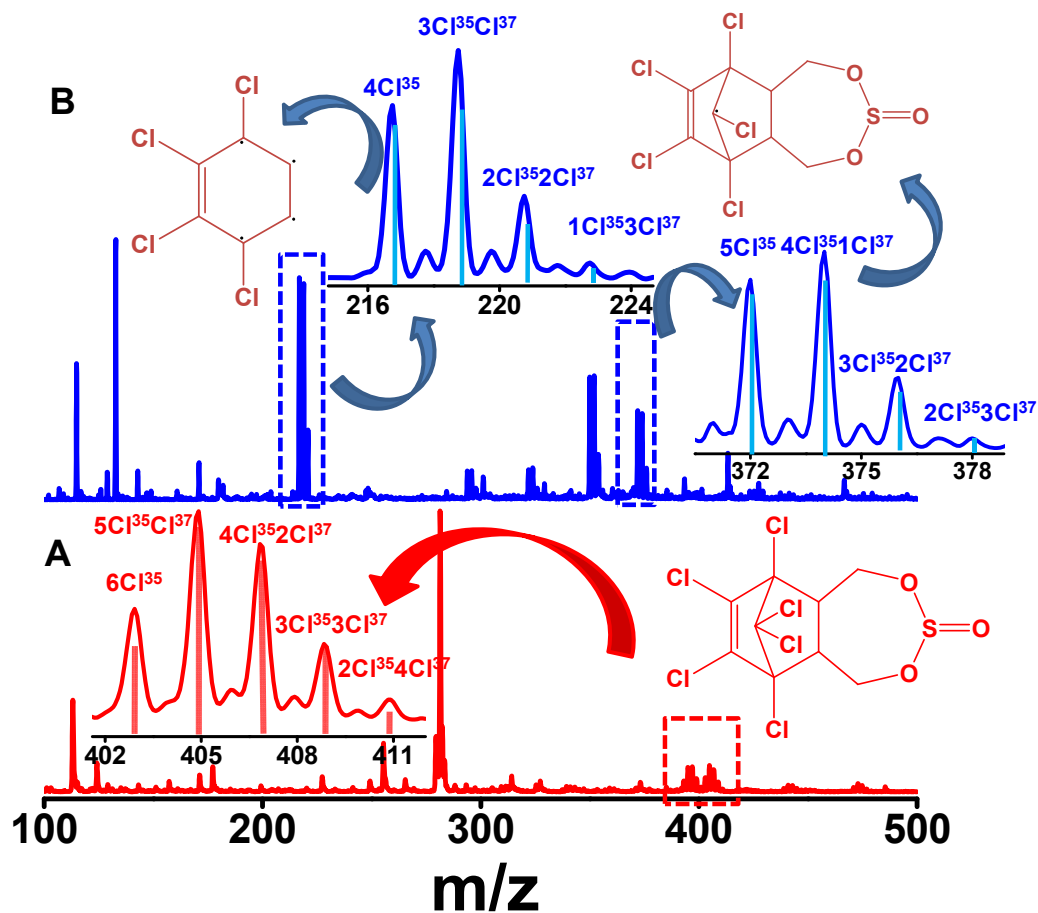


Fig. S6: A) ESI MS of ES showing the molecular ion peak at m/z 404 and B) the solution after reaction with RGO@Ag showing the fragmented product of ES in water showing the presence of peaks at m/z 372 and 219, respectively along with the isotopic distribution and probable structures. Isotope distribution is indicated on the spectrum.

Supplementary data S7

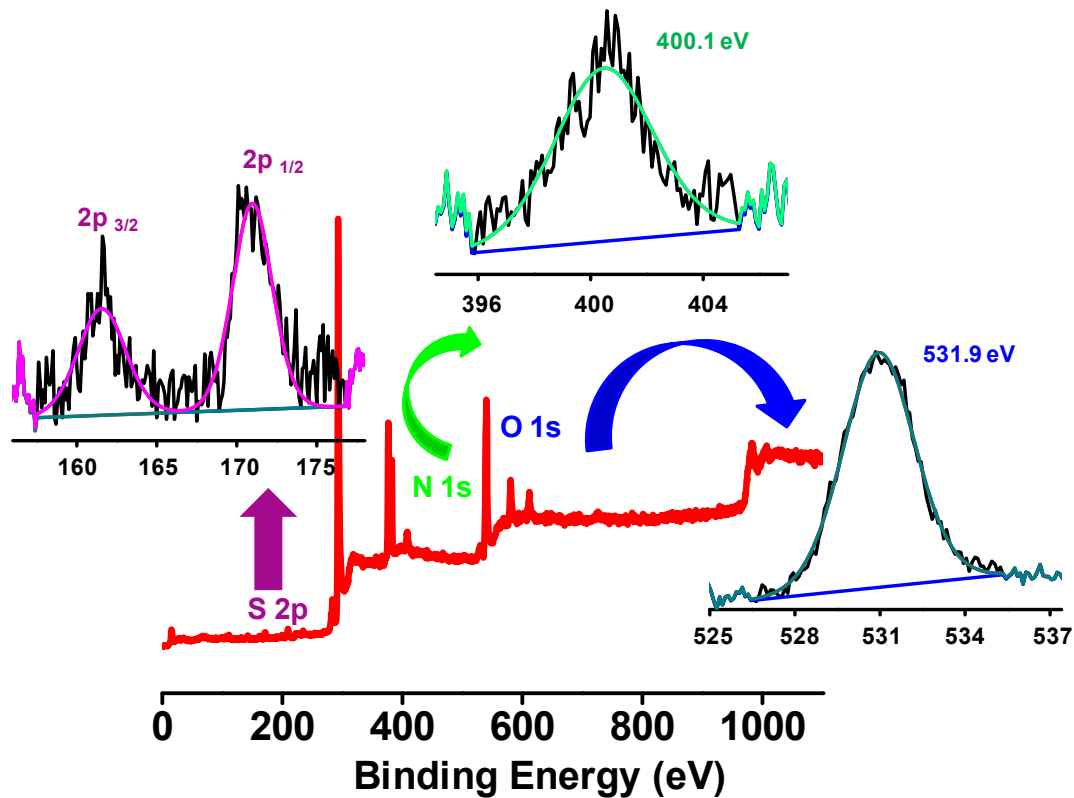


Fig. S7: XPS survey spectrum of the RGO@Ag composite after the reaction with CP. The inset showing the deconvoluted spectrum of O1s centred at 531.9 eV and N1s centered at 400.1 eV. Also shown is S2p, exhibiting two features at 162.0 and 171.0 eV. The peak at 162.0 eV for S2p_{3/2} assigned to +II oxidation state of sulphur.

Supplementary data S8

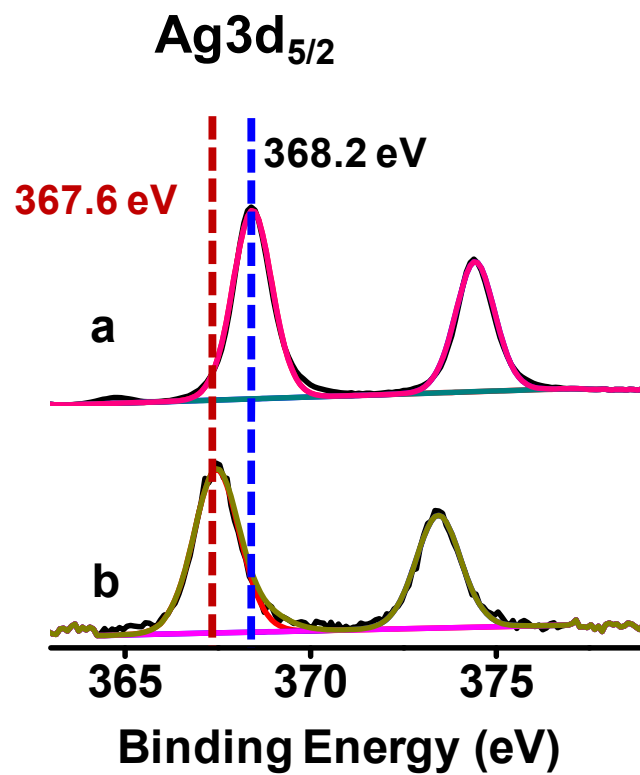


Fig. S8: Deconvoluted XPS spectrum of Ag in a) RGO@Ag (before reaction) and b) RGO@Ag after reaction with CP. Note that in Ag, the +1 oxidation state shifts 3d to a lower binding energy.

Supplementary data S9

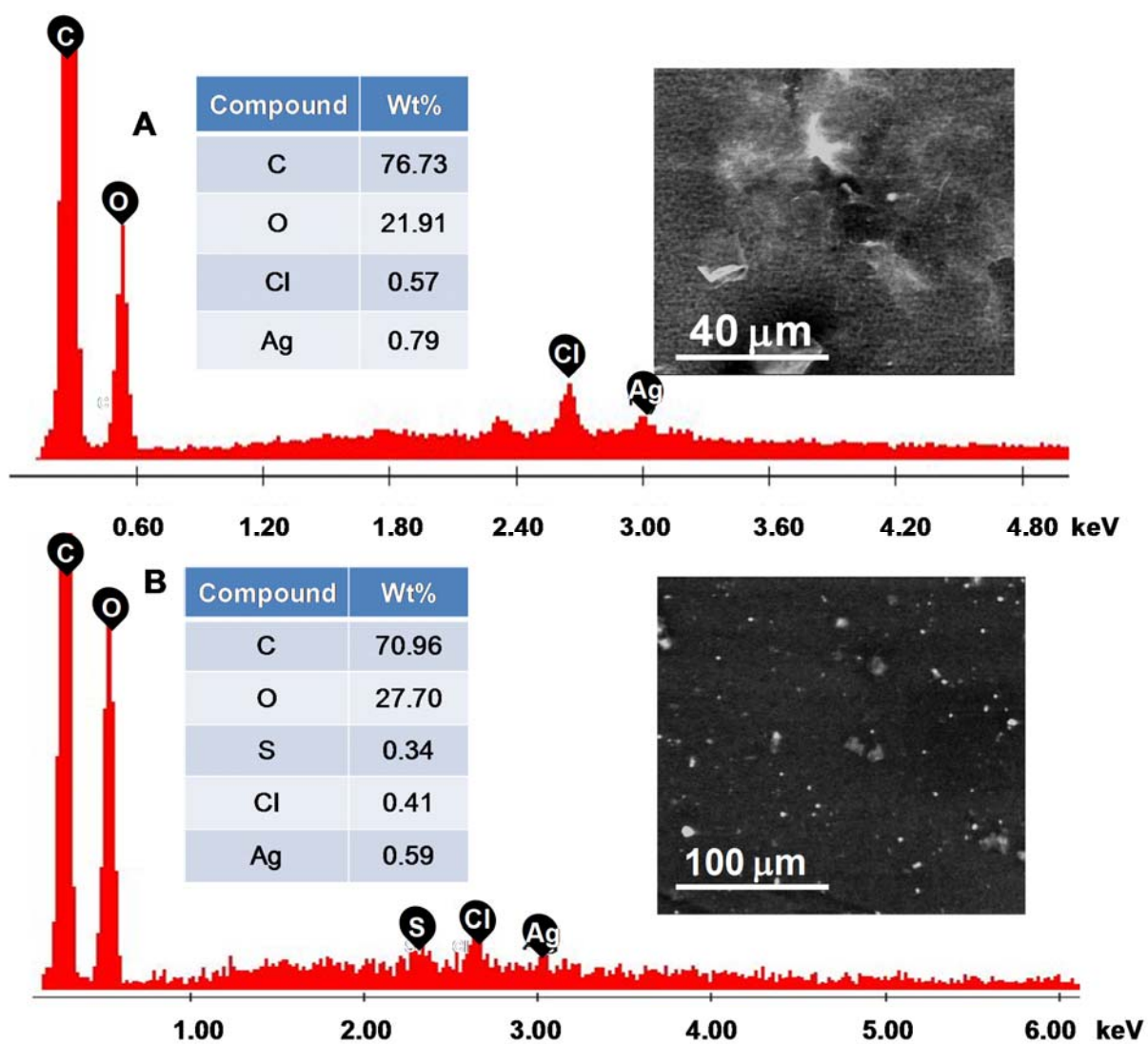


Fig. S9: SEM-EDS of RGO@Ag composite after the reaction with A) DDE and B) ES. The corresponding SEM images and the elemental ratios are given in the inset.

Supplementary data S10

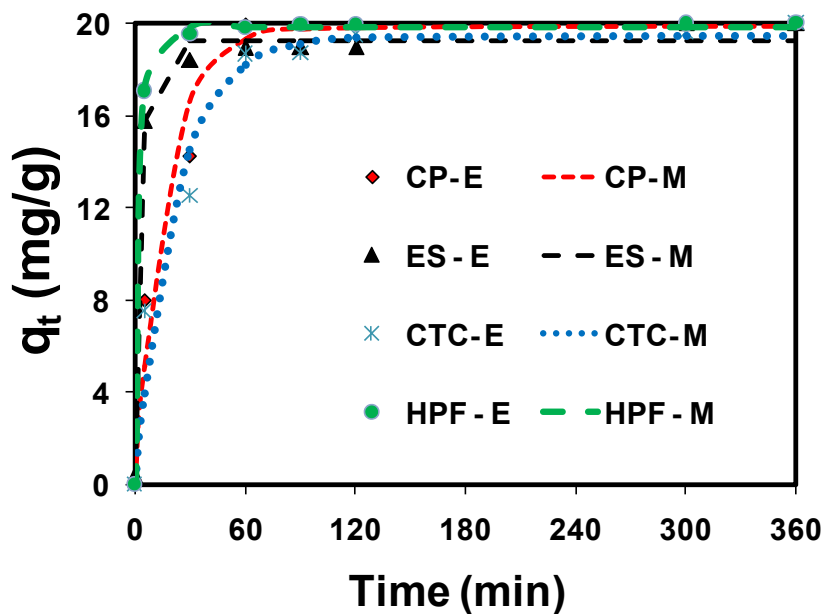


Fig. S10: Pseudo-first-order kinetic plots for the adsorption of pesticides by RGO@Ag composites.

Table S1: Estimated pseudo-first-order rate parameters.

Pollutants	k_1 (L/min)	q_e (mg/g)	RMSE	χ^2
CP	0.0603	19.8400	1.3250	1.9120
ES	0.3450	19.2200	0.5060	0.1070
CCl ₄	0.0455	19.4700	1.4670	3.4740
HFP	0.3910	19.8700	0.1360	0.0070

Supplementary data S11

Table S2: The maximum removal capacity of the RGO@Ag composite for different pollutant in mg/g.

Pesticides	Peak position (min)	Intensity (0 min)	Intensity (5 min)	Intensity (30 min)	Intensity (300 min)	Maximum Removal Efficiency (mg/g) of composite
Chlorpyrifos	12.2	115	75	36	0	765
Endosulfan	13.4	70	15	5.6	0	662
DDE	13.7	71	11	5.4	0	631
Carbon tetrachloride	2.3	200	125	75	4	997
Chloroform	2.1	30	23	19	4.1	132
Dichloromethane	2	26	16	9.2	3.4	121
1,1,1,3,3,3-hexa fluoro-2-propanol	2.4	750	105	16	0.8	1534
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hepta deca fluoro - 10-iodo decane	4.0	60	26	17	1.3	498