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Electronic Supporting Information

Formic Acid-Powered Reusable Autonomous Ferrobots for Efficient Hydrogen Generation under Ambient Condition

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1. Vibrating sample magnetometry (VSM) measurements

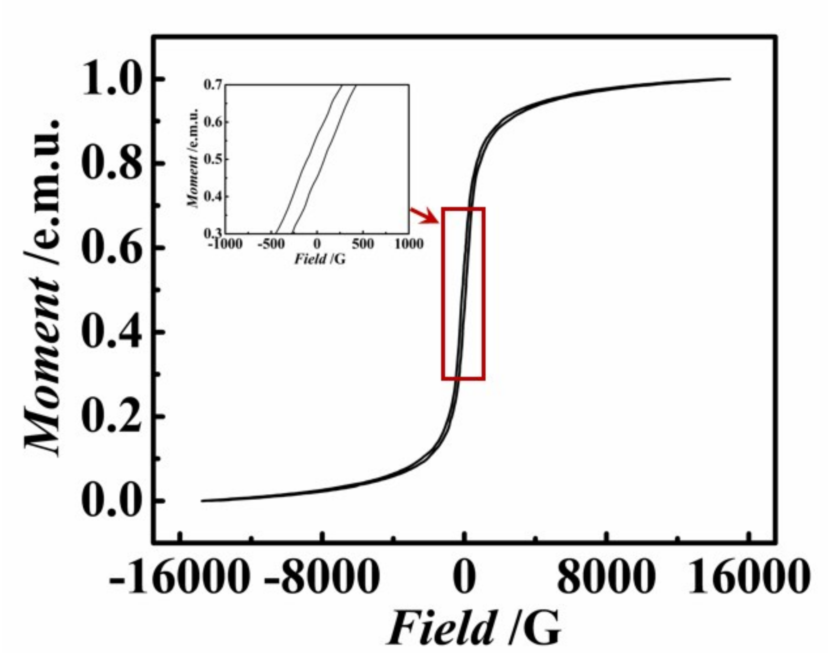

Figure S1. Vibrating sample magnetometry (VSM) hysteresis loop of freshly prepared ferrobots.

Figure S1 shows the magnetization curve was obtained from the VSM at 25ºC by varying the magnetic field from −15 to 15 kOe. The magnetization curve suggested that the ferrobots were soft ferromagnetic in nature.[1]

2. The calibration plot for hydrogen generation

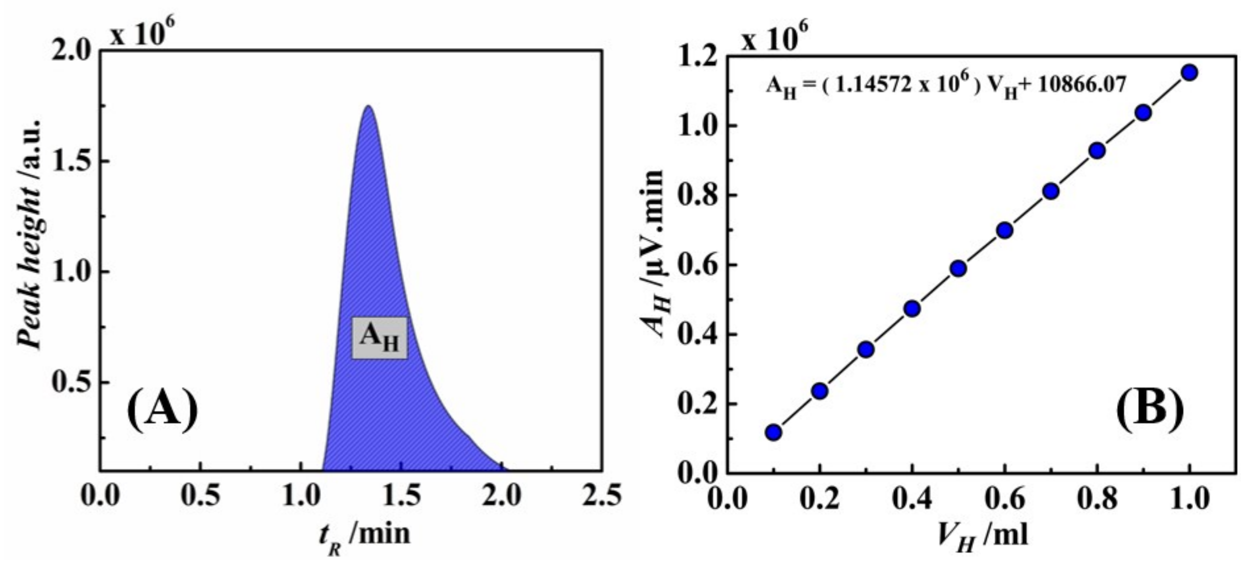

Figure S2. **(A)** Pure hydrogen (H_2) gas peak from the Gas Chromatography (GC). The peak at retention time (t_R) ~1.3 min represent hydrogen gas. The blue colored area inside the plot represents the area under the curve for the H_2 (A_H) gas **(B)** The calibration plot for H_2 gas.

Figure S2A shows the gas chromatography (GC) analysis of pure hydrogen (H_2) as reference gas. A Bruker 450 GC gas chromatography was equipped with Varian capillary column [CP – Wax52, packing: Carbosieve SII (80 – 100 mesh), dimension 1.80 m × 1/8" × 2.0 mm stainless steel, maximum temperature: 225°C] and thermal conductivity detector (TCD).[2] The injector, oven, and detector temperatures were fixed at 100°C while the carrier gas nitrogen was flown at 10 ml/min. For a particular volume of H_2 gas, a GC peak with a well-defined area under the curve (A_H) for the retention time in the range of 1 min – 2 min was obtained. A calibration curve for pure H_2 gas was obtained by injecting different volumes of pure H_2 gas (0.1 ml – 1 ml) into the TCD port of the GC. **Figure S2B** shows the linear correlation between the volume of pure hydrogen gas (V_H) with corresponding area under the curve as, $A_H = (1.14572 \times 10^6)\ V_H \pm 10866$. After obtaining the V_H versus A_H calibration for pure H_2, the gaseous products issuing out of ferrobot-FA reaction at varying parameters were analyzed in GC under same condition.

3. Characterization of iron (II) formate

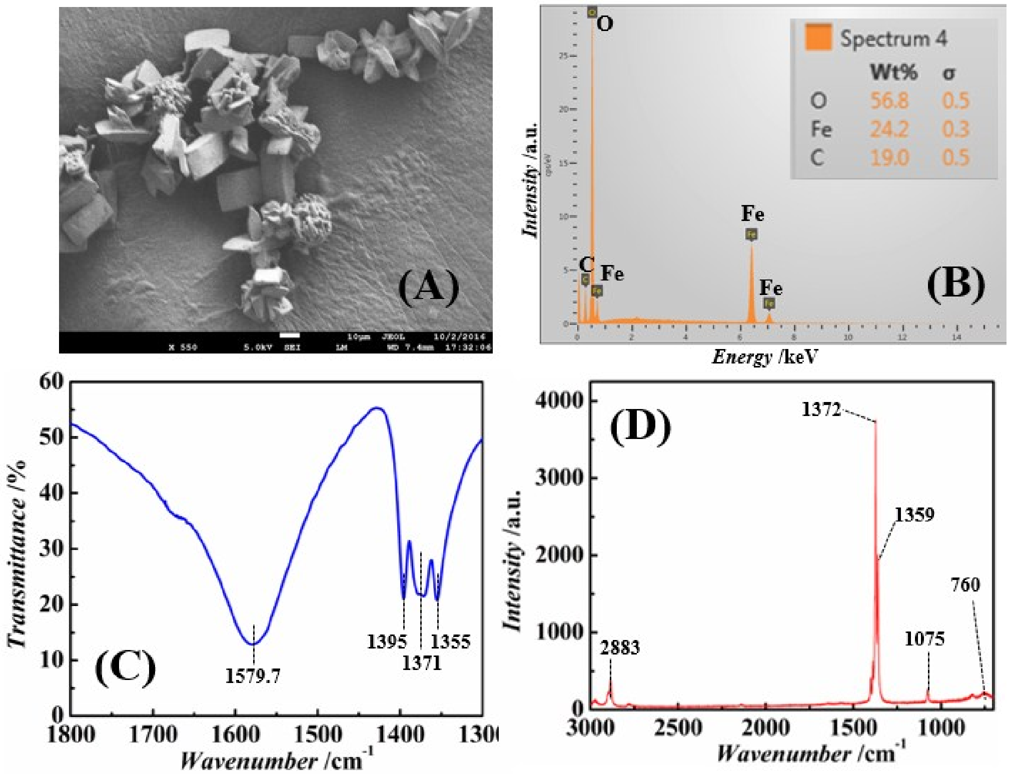

Figure S3. **(A)** Field emission scanning electron microscopy (FESEM) image **(B)** Energy Dispersive X-ray (EDX) **(C)** Fourier Transform Infrared (FT-IR) spectrum and **(D)** Raman spectrum of the iron (II) formate. The scale bar at the bottom is of 1 µm.

The FESEM image **Figure S3A** shows the as formed iron (II) formate salt crystals. The crystals were mostly elongated hexagonal in shape. The EDX of the sample shows the presence of elemental iron (Fe), oxygen (O), and carbon (C) peaks **(Figure S3B)**. The **Figure S3C** shows the FT-IR plot of iron (II) formate. The carboxylic acid salts show strong characteristic band in the region 1650-1550 cm^{-1} due to asymmetric stretching vibration of the group COO. The symmetric stretching vibration of COO gives rise to a medium intensity band in the range 1440-1335 cm^{-1} and generally has two or three peaks.[3] The peak at 1371 cm^{-1} is identified as the characteristic symmetric COO stretch, while the peak at 1579 cm^{-1} is the characteristic asymmetric OCO stretch of the formate species. Two additional positive peaks, 1355 cm^{-1} and 1395 cm^{-1}, were observed near the 1371 cm^{-1} peak which can be attributed to the weaker signal to the C−H bending mode. No bands were observed for the υ(C=O) stretch in the region around 1700 cm^{-1}, which was expected for the unbound (C=O) in the intact HCOOH molecules.[4] Thus, FTIR spectrum confirmed the upright bidentate orientation of the absorbed formate ion on the FeNP surface. A broad peak around 3200-3220 cm^{-1} region (not shown in the plot) was attributed to O-H vibration band of the water molecules. The **Figure S3D** shows the Raman plot of iron (II) formate. The peaks at 1359 cm^{-1} and 1372 cm^{-1} in the Raman spectrum represents the symmetric C-O stretching and in-plane C-H bending respectively, while the peak at 1075 cm^{-1} is assigned to the out-of-plane C-H bending mode of the formate species. The asymmetric C-O stretching peak, which should have appeared at 1580 cm^{-1} was not observed in Raman spectrum probably due to its very weak intensity. The weak intensity peaks at 760 cm^{-1} in Raman plot corresponds to the symmetric O-C-O bending mode. The absorptions at 2883 cm^{-1} in Raman plot corresponds to the C-H symmetric stretching.[5,6]

Confirmatory test for ferrous (Fe^{2+}) ion: When 4-5 drops of 0.1 M ammonium thiocyanate (CNS^- ion) was added to 0.05 g of the sample and mixed in a test tube, the characteristic intense blood-red coloration was not formed thus confirming the absence of Fe^{3+} in the sample, thereby indicating that the sample is a ferrous salt.[7] Furthermore, when 2-3 drops of 0.1 M potassium ferricyanide was added to the sample, the blue precipitate (Turnbull's blue) of ferrous ferricyanide was formed, thereby re-confirming the presence of Fe^{2+} ions.[7]

Lime water test: The lime water experiment[7] suggested that the evolved gas does not contain carbon dioxide (CO_2) gas, thus negating the possibility of FeNP-mediated catalytic decomposition of FA ($HCOOH = CO_2 + H_2$) at room temperature.

4. Reaction of iron and iron oxides with formic acid

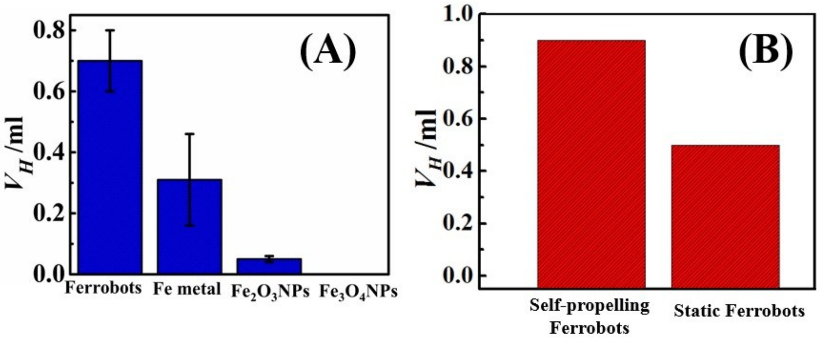

Figure S4. **(A)** The plot shows the volume of liberated H_2 (V_H) gas when 0.2 g of various samples immersed in 15% (v/v) FA solution for 1 min. **(B)** The plot shows the volume of liberated H_2 (V_H) gas when 0.05 g of self-propelling and static ferrobots were immersed in 2 ml of 15% (v/v) FA solution for 2 min.

About 0.2 g of iron (Fe) metal powder, ferrobots, haematite nanoparticle (Fe_2O_3NPs), and magnetite nanoparticles (Fe_3O_4NPs) were immersed in 1.5 ml of 15% (v/v) formic acid (FA) solution for 1 min at room temperature and the volume of evolved gas was collected and analysed in GC. **Figure S4A** shows the plot show the volume of liberated H_2 (V_H) gas for various samples at room temperature. Further experiments were carried out to investigate the effect of ferrobot motion on hydrogen evolution.[8] About 0.05 g of ferrobots were immersed in two Eppendorf tubes containing 2 ml of 15% (v/v) formic acid (FA) solution in each of them for 2 min at room temperature and the volume of evolved gas was collected and analysed in GC. In one set of experiment, the ferrobots were allowed to self-propel in FA solution and in another set, the ferrobots were made stationary by placing a magnet beneath the tube, thereby restricting its motion. **Figure S4B** shows the plot show the volume of liberated H_2 (V_H) gas for both the samples at room temperature.

5. Experimental set-up for chemotaxis studies

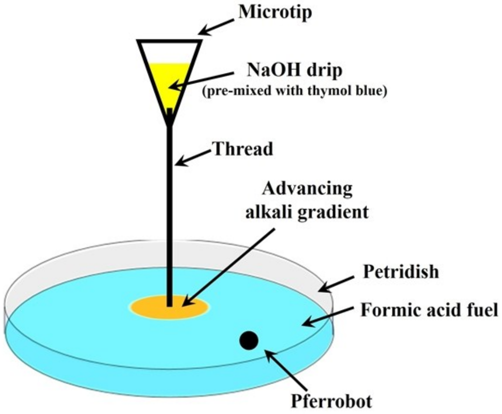

Figure S5. Experimental set-up to study the chemotaxis of a Pferrobot in response to imposed alkali trigger.

Figure S5 shows experimental setup employed to characterize the chemotactic behaviour of the motors.[1] A micropipette tip was used as a NaOH reservoir while the formic acid fuel was placed on a petridish. The advancing alkali front was observed using thymol blue indicator in the formic acid bath. The Pferrobot was placed away from the thread to capture its motion towards the alkali trigger.

6. Regeneration of ferrobots

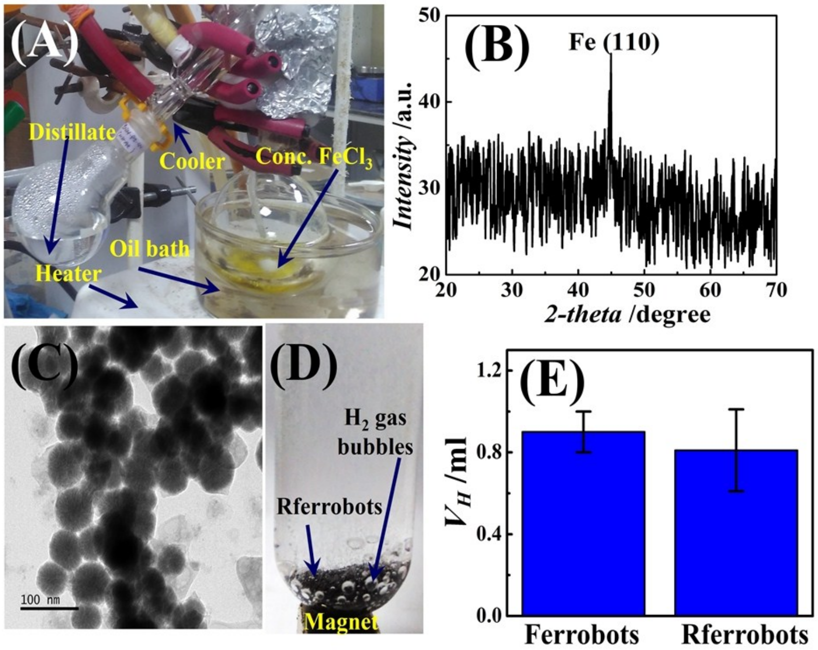

Figure S6. **(A)** Distillation set-up and the sample collection after 2 h. The obtained colourless distillate consists of FA, water and unreacted HCl, and the flask inside the oil bath contains (yellow in colour) concentrated $FeCl_3$ solution (yellow in colour). **(B)** XRD pattern and **(C)** TEM image of the regenerated ferrobots (Rferrobots). The scale bar in the TEM image is of 100 nm. **(D)** The image shows the reaction between Rferrobots (black particles, 0.05 g) with 10 ml of 15% (v/v) formic acid solution at room temperature. **(E)** The plot shows the volume of liberated H_2 (V_H) gas when 0.05 g of ferrobots and Rferrobots were immersed in 2 ml of 15% (v/v) FA solution for 2 min.

Initially, 1.5 g of ferrobots were immersed in 2 ml 15% formic acid (HCOOH, FA) in a 5 ml glass beaker. The beaker was left undisturbed for 30 min at room temperature to ensure the completion of the reaction. The ferrobots react with FA resulting in formation the iron (II) formate ($Fe(HCOO)_2$) salt and H_2 gas through the chemical reaction: $Fe (s) + 2HCOOH (l) + 2H_2O = H_2 (g) + Fe(HCOO)_2.2H_2O (s)$.[9,10] After 30 min, ice cold absolute ethanol was added in order to precipitate the metal formate, as metal formates were insoluble in ethanol. Once again, the beaker was left undisturbed for 40 min at room temperature. The greyish white precipitate of iron (II) formate was collected and washed thrice with ethanol and vacuum dried overnight to remove the moisture content. The finer iron (II) formate precipitate slow high tendency to oxidation in air.

For regeneration experiments, 0.5 g of iron (II) formate powder was left exposed to air for 1 h, resulting in oxidation of greyish white iron (II) formate to yellowish brown iron (III) formate. The as obtained iron (III) formate powder was dissolved in 40 ml of 20% (v/v) hydrochloric acid (HCl) and heated for 20 min at 80^{o}C. After 20 min, the solution turned yellow in colour due to the formation of ferric chloride ($FeCl_3$) through the chemical reaction: $Fe(HCOO)_3$ (s) + 3HCl (l) = $FeCl_3$ (s) + 3HCOOH (l). The yellow solution was transferred into 50 ml round bottom flask and was subjected to simple distillation at 101˚C for 3 h. The **Figure S6A** shows the typical distillation set-up and collection of the samples after 2 h. The obtained distillate consists of FA, water and unreacted HCl and the flask inside the oil bath consists of concentrated $FeCl_3$ solution. The FA and unreacted HCl present in the distillate can be separated from each other using hydrochloric acid-formic acid-water-methyl isobutyl ketone system reported by McAteer *et al.*[11] and the obtained FA can be reused as fuel for hydrogen generation.

The ferrobots were regenerated from the as obtained concentrated $FeCl_3$ solution. For this purpose, 1 ml of concentrated $FeCl_3$ solution was added dropwise into 2 M sodium borohydride ($NaBH_4$) solution (10 ml) with vigorous stirring at 1200 rpm. The addition of $FeCl_3$ in $NaBH_4$ solution resulted in immediate formation of black coloured FeNPs. The FeNPs were collected using a magnet and washed thrice with ethanol followed by vacuum drying in an oven at 60˚C. The **Figure S6B** and **Figure S6C** shows the XRD plot and TEM micrograph of the regenerated ferrobots (Rferrobots) respectively. The XRD plot exhibited the characteristic peak of a BCC α-Fe with principal plane (110) at $2\theta = 44.7^{o}$ (JCPDS 06-0696), which indicated the presence of zero-valent iron.[1,12] The TEM images clearly suggests that the ferrobots consists of FeNP aggregates. The TEM revealed that these aggregates were composed of discrete spherical FeNPs of diameter 80 nm or less. The **Figure S6D** shows that immersed Rferrobots reacts with 10 ml 15% (v/v) FA solution inside a test tube to liberate H_2 gas bubbles owing to its reaction with aqueous FA fuel. Further experiments were carried out to compare the efficacy of Rferrobots with ferrobots for hydrogen evolution. About 0.05 g of Rferrobots were immersed Eppendorf tube containing 2 ml of 15% (v/v) formic acid (FA) solution for 2 min at room temperature and the volume of evolved gas was collected and analysed in GC. All experiments were performed thrice and the error bars represent standard deviation. **Figure S6E** shows the plot show the volume of liberated H_2 (V_H) gas for ferrobots and Rferrobots at room temperature. The Rferrobots demonstrate similar efficiency for hydrogen generation from FA fuel compared to ferrobots.

7. Supporting Video details

Video S1: The video shows the respective reaction between iron (Fe) metal powder, ferrobots, haematite nanoparticle (Fe_2O_3NPs) and magnetite nanoparticles (Fe_3O_4NPs) and 15% (v/v) formic acid (HCOOH, FA) solution at room temperature. A magnet was placed at the bottom of the tube in order to immobilize the samples for better visibility of the evolved gas from the sample's surface.

Video S2: The video shows the respective reaction between motile and stationary ferrobots with 15% (v/v) formic acid (HCOOH, FA) solution at room temperature.

Video S3: The video shows the chaotic migration of a ferrobot (~ 5 μm size) inside 15% (v/v) formic acid (FA) solution. The spontaneous generation of hydrogen (H_2) bubbles due to the reaction between FeNPs and aqueous FA fuel resulted in self-propulsion the motor inside FA fuel.

Video S4: The video clip shows the magnetically-guided motion of a ferrobot (~5 μm) inside 15% (v/v) formic acid (FA) fuel in a straight-line trajectory.

Video S5**:** The video clip shows the steering of the self-propelling ferrobot in inside 15% (v/v) formic acid (FA) solution with the help of a bar magnet.

Video S6**:** The video clip demonstrates the chemotaxis of a Pferrobot in formic acid bath. The motor moved towards a NaOH source under an alkali gradient. The alkali gradient was tracked by thymol blue indicator, which turned form blue to yellow and from yellow to pink as the NaOH front moved from the centre to the sides of the glass petridish.

Video S7: The video clip shows the controlled chemo-magneto taxis of a Pferrobot inside a microchannel under the coupled influence of the internal alkali gradient and the external magnetic field. The motor moved towards the thread from a higher to lower formic acid concentration region while it moved away from the thread in the opposite direction when migrated under the influence of an external magnet.

Video S8**:** The video clip shows the ferrobot mediated co-generation of H_2 and O_2 gases and real-time production of electrical energy by Proton-exchange membrane fuel cell (PEMFC) for powering an electric fan.

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