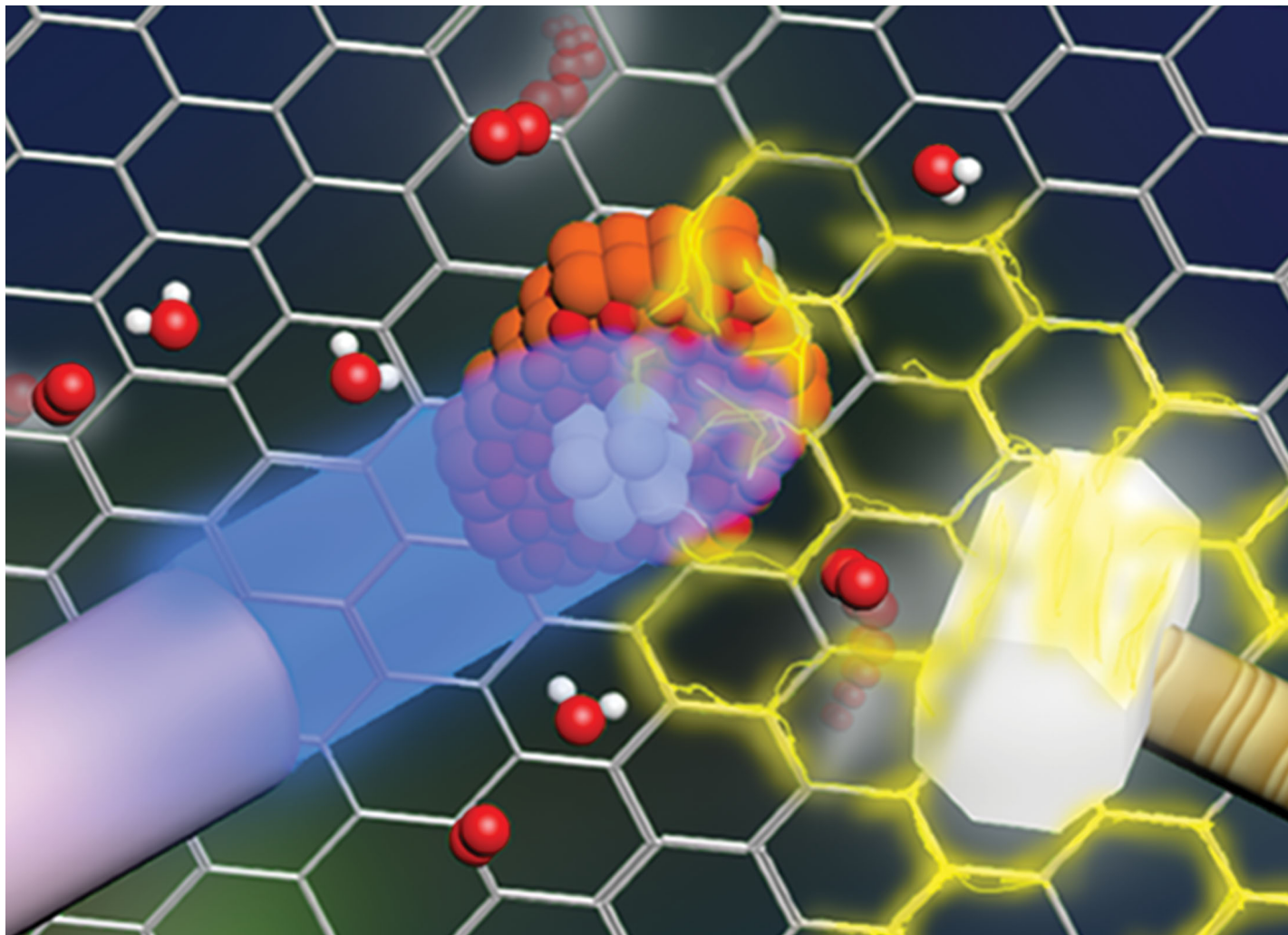




Showcasing research from Chun-Hu Chen research group at National Sun Yat-Sen University, Taiwan. Image designed and illustrated by Joey Andrew A. Valinton and Ren-Huai Jhang.

Heterojunctions of silver–iron oxide on graphene for laser-coupled oxygen reduction reactions

Laser irradiation coupled with electricity towards Ag/Fe₂O₃ heterojunction on N-doped graphene achieves kinetically-balanced oxygen reduction reaction (ORR) and suppressed formation of corrosive H₂O₂. Bandgap excitation of Fe₂O₃ and plasmonic hot electrons of Ag synergistically enhances laser-coupled ORR performance.

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Heterojunctions of silver–iron oxide on graphene for laser-coupled oxygen reduction reactions†

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We report a two-step hybridization of N-doped graphene and Ag-decorated Fe₂O₃ hematite to realize a balanced oxygen adsorption/desorption equilibrium and a laser-coupled ORR (LORR). The stable plateau currents with *n* values of 3.9 in a wide potential range (0.2–0.7 V) and 7.5% peroxide inhibition of the LORR are found to be directly associated with the Ag/Fe₂O₃ heterojunction, where interactions of semiconductor band gap excitation and plasmonic resonance-induced hot electrons are proposed to occur.

Great efforts in searching for substitutes of Pt/C as inexpensive oxygen reduction reaction (ORR) electrocatalysts have been extensively applied for modern fuel cells and metal–air batteries.¹ Iron oxide catalysts exhibiting high abundance, excellent stability, and low environmental impact are promising alternatives to Pt/C. However, like other low-cost metal oxides, they suffer from weak energy densities and a two-electron transfer ORR, which generates corrosive peroxide species.² Apparently, combining them with mesoporous carbon materials has been reported to successfully improve the number of transferred electrons during reduction,³ although achieving a stable limiting current remains elusive due to sluggish kinetics produced by a low electrocatalytic conversion.⁴ Efficient kinetics of both oxygen adsorption/desorption needs to be achieved to address this issue.

According to the volcano curves of ORR activity, the function of oxygen binding energy over various species,⁵ iron can facilitate catalytic O–O bond breaking due to strong oxygen adsorption, but this property hampers the ORR catalytic cycle because the desorption of the as-yielded intermediates/products from the occupied sites becomes difficult. Silver, on the other hand, possesses a relatively weak oxygen adsorption affinity,⁶ which

benefits intermediate/product elimination, but O₂ immobilization for effective catalysis becomes difficult. Our rational design aims to establish a well-balanced ORR system by establishing the interfacial combination of Ag and Fe, which promotes complementary and synergistic activities. Compared to platinum, the abundance and cost of silver are reasonable for commercial usage despite its low electron-transfer (*n*) values and high initial voltage losses.⁷

Recent studies demonstrated that photo-assisted ORRs are critical to realize light-driven fuel cells.⁸ Chen and coworkers further revealed the mechanisms *via* which Ag–Pt nanocages can inhibit peroxides through plasmon-induced hot electrons.⁹ Strong surface plasmons can only be observed in noble metals and are commonly absent in metal oxide materials. Hence, noble metals become the usual materials considered for light-assisted ORR studies.¹⁰ Exploration of the usage of alternative light-excitation routes on low-cost metal oxide materials towards enhancing the ORR is highly desirable but less established. In addition, white, continuous light sources were commonly used in the reported photo-assisted ORR,^{9,10} however, achieving specific excitation remains difficult as the identification of active sites remained uncertain. We thus adopted a laser as the light source with a very narrow bandwidth to realize specific excitation, and a smaller required power input due to the beam-concentrated nature of the laser.

In this work, we report a two-step synthesis to produce Ag/Fe₂O₃/N-doped graphene nanocomposites (Ag/FNG) with the controlled formation of a Ag/Fe₂O₃ heterojunction. Significantly improved ORR activity (*n* = 3.9) and efficient kinetics with a stable limiting current can be obtained, both of which were established to originate from the heterojunction sites. For the first time, these composite catalysts demonstrated their photoactivities towards peroxide suppression through a laser-coupled ORR (LORR), a light-electricity co-activation process on the electrocatalysts.

Ag/FNG was prepared by refluxing a mixture of iron(II) acetate and graphene oxide (GO) in dimethylformamide (DMF), followed by the addition of silver nitrate (10% of the moles of iron) and a subsequent hydrothermal treatment at 150 °C. Subsequently, the

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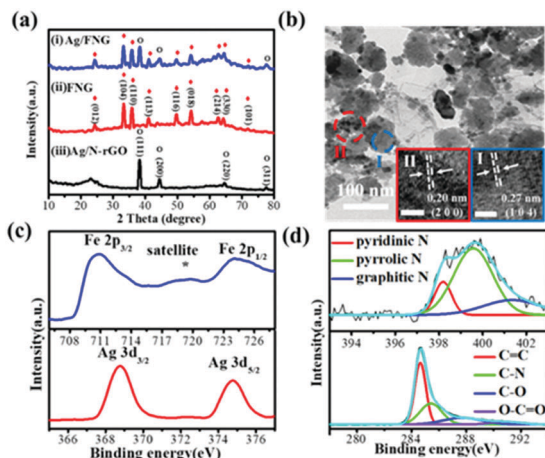


Fig. 1 Characterization of the Ag/FNG nanocomposites. (a) The comparison of the XRD patterns of the nanocomposites. The red diamonds and open circles correspond to the phases of hematite Fe_2O_3 and metallic Ag, respectively. (b) The TEM image of Ag/FNG. The inset high-resolution images correspond to the circle areas labelled as I and II. The scale bars in the insets have a measure of 2 nm. (c) The XPS data of Ag 3d and Fe 2p; and (d) C 1s and N 1s.

control samples of $\text{Fe}_2\text{O}_3/\text{N}$ -doped graphene (FNG) and Ag/N-rGO were prepared similarly without the Ag and Fe precursors, respectively. The XRD patterns of Ag/FNG correspond to hematite Fe_2O_3 and metallic silver (Fig. 1a), confirming the deposition of metallic Ag rather than Ag^+ doping in the iron oxide frameworks.¹¹ The XRD results of the control samples FNG and Ag/N-rGO agree with their hematite and Ag components, respectively. The morphology of Ag/FNG according to the acquired TEM image resembles the deposition of finer particles (diameter 15.3 ± 0.7 nm) onto the surface of larger, distinct ones (diameter 79.3 ± 11.6 nm) supported by the graphene sheets (Fig. 1b). These particles were confirmed to be iron and silver by EDXS data (Fig. S1, ESI[†]), where the corresponding molar ratio according to ICP-MS is 0.139, a slightly higher value than that of the precursor mixture. The HR-TEM characterization of the large particles (Fig. 1b-I) shows 0.27 nm lattice fringes corresponding to d_{104} of hematite Fe_2O_3 . Meanwhile, the observed 0.20 nm lattice fringes on the finer particles (Fig. 1b-II) agree with d_{200} of Ag. These results clearly demonstrate the successful formation of the discrete Ag/ Fe_2O_3 heterojunction in Ag/FNG, highly preferred for the effective exposure of Ag-to-Fe interfaces. The XPS studies (Fig. 1c) show the binding energies of Fe $2p_{3/2}$ and $2p_{1/2}$ to be 711.5 and 724.5 eV, respectively, together with the presence of a satellite peak, corresponding to Fe(III).^{4c} Also, the binding energies of Ag $3d_{5/2}$ and $3d_{3/2}$ at 368.8 and 374.8 eV, respectively, further verify the presence of metallic Ag.¹² The C 1s spectra indicate the reduction of graphene oxide (rGO) in Ag/FNG, while N 1s deconvolution indicates nitrogen doping in rGO with graphitic (~ 401.6 eV), pyrrolic (~ 399.5 eV), and pyridinic (398.2 eV) forms (Fig. 1d), which is known to greatly enhance the ORR activity.¹³ We selected DMF, an N-containing organic solvent, for the possible formation of iron-DMF coordination complexes capable of achieving higher degrees of N doping in GO (N-rGO) which cannot be accomplished using the conventional ammonia addition approach.^{13b}

The ORR performance of Ag/FNG and the control samples was evaluated through cyclic voltammetry (CV) plots under O_2 - and N_2 -saturated alkaline solutions (Fig. 2a). The results reveal that Ag/FNG possesses the largest current and most positive onset potential at 0.92 V (vs. RHE) as compared to Ag/N-rGO (0.87 V), FNG (0.86 V), and Fe_2O_3 (0.70 V). Fe_2O_3 has a much more negative onset potential than FNG supporting the effective ORR enhancement due to N-rGO hybridization. In Fig. 2b, the linear scan voltammogram (LSV) curves of Ag/FNG demonstrate plateau currents starting at 0.6 V. The curve shapes of Ag/FNG, as well as the control samples (Fig. S2, ESI[†]), remain consistent as the rotation speeds are increased (400–2025 rpm), which enables more O_2 to reach the electrode surface. Ag/FNG provides a greater increase in the current density as compared to others while maintaining a plateau-like diffusion limiting curve. This means that the catalyst is active enough to achieve higher conversion and faster diffusion kinetics. Ag/FNG demonstrated superior ORR activity and mass transport compared to the ones without the Ag/ Fe_2O_3 heterojunction.

The comparison of the LSV and the number of electron transfer curves among the control samples is shown in Fig. 2c and d, respectively. The two-step LSV curves of Fe_2O_3 suggest two different ORR stages in the range of 0.4–0.7 V, where the two-electron transfer pathway governs the ORR at potentials above 0.6 V (Fig. 2d). Compared to Fe_2O_3 , FNG shows a similar two-step LSV curve but, at 0.3 V, it produces higher n values (3.78) and currents. N-rGO hybridization with Fe_2O_3 enhances the current densities and decreases the onset potential barrier giving higher n values, suggesting the formation of Fe-N-C sites,¹⁴ as well as the quasi-four-electron ORR occurring from the combination of electrochemical two-electron reduction and chemical disproportionation with rapid mass transfer.¹⁵ However, the two-step-like LSV and the absence of limiting currents are still observed, similar to the reported graphene/iron oxide composites.^{3,4,16} In contrast, the single-step LSV with the

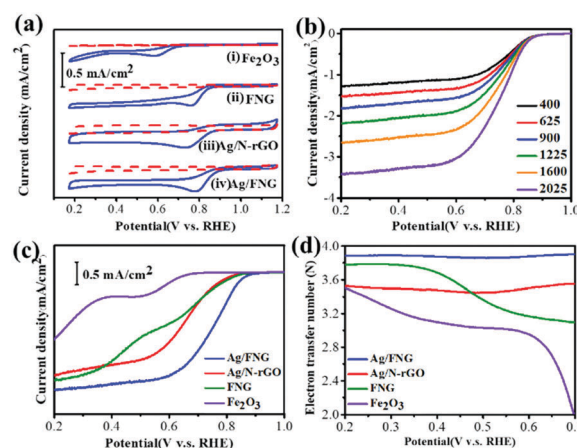


Fig. 2 The ORR studies of the Ag/FNG nanocomposites. (a) The CV comparison in 0.1 M aqueous KOH with N_2 -saturated (red dashed lines) and O_2 -saturated (blue solid lines) conditions. (b) The LSVs of Ag/FNG in O_2 -saturated 0.1 M KOH with varied rotation rates from 400 to 2025 (rpm). (c) The RDE comparison of Ag/FNG and the related samples at a rotation rate of 1600 rpm. (d) The electron transfer numbers of the samples in (c).

plateau current of Ag/FNG indicates a direct four-electron transfer similar to that observed in benchmark Pt/C. This similarity suggests that the plateau current can be presumably associated with the balanced adsorption/desorption equilibrium exhibited by Ag. Electrochemical Impedance Spectroscopy (Fig. S3, ESI†) shows that an increase in conductivity has been exhibited by Ag/FNG due to the presence of the Ag-decorated interface with Fe_2O_3 . The lowest charge transfer resistance of Ag/FNG among Ag/rGO and FNG further corresponds to the improved kinetics (Table S1, ESI†).

Ag/FNG exhibits the greatest n value of 3.9, which remains stable over a wide potential range (0.2–0.7 V), while Ag/N-rGO exhibits relatively low n values and more negative onset potentials. Note that both hematite and FNG also show much lower n values particularly at the high potential regions (0.6–0.7 V), indicating the essential role of the Ag/ Fe_2O_3 heterojunction in requiring only small potential bias to realize high n values. Also, Ag/FNG only requires around 10% (*i.e.* 11.88%) Ag to accomplish a significant ORR enhancement, which is smaller than prescribed in the literature.⁹ Moreover, Ag/FNG outperforms similar electrocatalysts (Table S2, ESI†), emphasizing the formation of Ag/ Fe_2O_3 interfaces on graphene as an effective strategy to achieve a low-cost Pt/C replacement.

To study the role of the Ag/ Fe_2O_3 heterojunction, an analogous control sample without Ag/ Fe_2O_3 interfaces was synthesized to compare its behavior with Ag/FNG (see the ESI†). The acquired TEM image shows that the Fe_2O_3 particles have no attachment with the fine Ag dots (~ 5 nm, labeled by red arrows in Fig. 3a) on graphene. The XRD data confirm the presence of both metallic Ag and hematite (Fig. S4, ESI†). The LSV results (Fig. 3b) are comparable to the two-step ORR observed in FNG, while the n values are similar to that of Ag/N-rGO (at 0.5–0.7 V, see Fig. 3c). Therefore, the electrocatalytic properties in this heterojunction-free catalyst sufficiently prove that the plateau current of Ag/FNG is due to the presence of the Ag– Fe_2O_3 heterojunction. Also, the selective removal of the Ag nanoparticles from Ag/FNG (named as Ag/FNG-Ag etched in Fig. S5, ESI†) replaces the features of plateau currents, most positive onset potentials, and high n values as observed in Ag/FNG with those of FNG. These results clearly

confirm that the Ag– Fe_2O_3 heterojunction is responsible for the greatly enhanced ORR performance.

Smaller Ag particles are generally known to exhibit greater ORR activity.¹⁷ To investigate whether the Ag nanoparticles may solely act as the main active sites responsible for the enhanced ORR, we further narrowed down the Ag particle size in Ag/N-rGO for comparison. As shown in Fig. 3d, the Ag/N-rGO prepared under surfactant cetyltrimethylammonium bromide (CTAB) conditions, denoted as Ag/N-rGO-CTAB, yields a smaller Ag particle size (5.43 ± 2.25 nm) than Ag/N-rGO. Ag/N-rGO-CTAB exhibits a more positive ORR onset potential (0.89 V, see Fig. 3e) and a slightly smaller n value (Fig. 3f) as compared to Ag/N-rGO. These results suggest that the ORR activity of Ag/FNG cannot depend only on the Ag particles, although Ag is critical to gain improved kinetics. Therefore, the Ag/ Fe_2O_3 heterojunction is mainly responsible for the synergistic ORR enhancement in Ag/FNG.

We further explore the photoelectrochemical ORR of Ag/FNG under the direct laser irradiation penetrating massive water medium at room temperature (see the ESI†), where drastic local heat and temperature increases at the electrodes are negligible to influence the ORR performance. The UV-vis spectra of Ag/FNG and the control samples were acquired first to identify the absorption energy among them (Fig. 4a). The band at 269 nm (labelled by the red zone) is due to the $\pi \rightarrow \pi^*$ transition of reduced graphene oxide,¹⁸ since all the samples that contain rGO possess this band but Fe_2O_3 . The shoulder band at 405 nm (labelled by the blue zone) can be attributed to the band gap absorption of Fe_2O_3 .¹⁹ The surface plasmonic absorption of the Ag nanoparticles is also observed in Ag/N-rGO within the blue zone.²⁰ Thus, the light source of a 405 nm laser used in this study can both stimulate the band gap excitation of Fe_2O_3 and the surface plasmon of Ag. Different from the reported light sources with continuous wavelengths,^{9,21} our studies of the

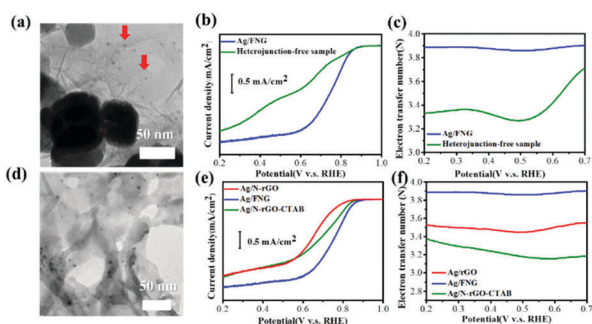


Fig. 3 The heterojunction influence on the ORR activities. (a) The TEM image of the Ag/ Fe_2O_3 heterojunction-free sample, and comparison of its RDE (b) and electron transfer number (c). (d) The TEM image of Ag/N-rGO-CTAB, and the comparison study of its RDE (e) and electron transfer number (f).

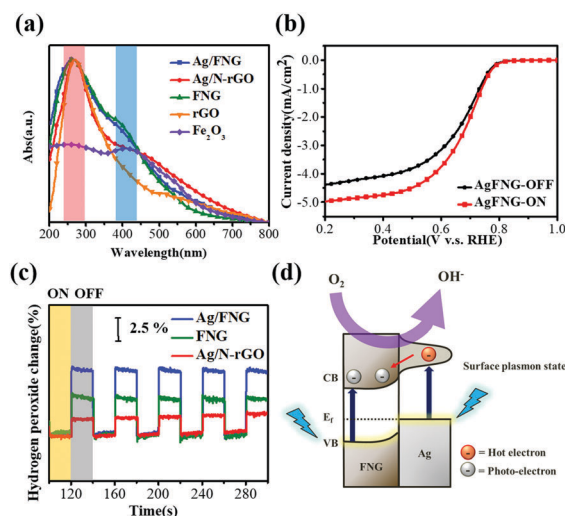


Fig. 4 LORR studies. (a) The UV-vis spectra of all the samples. (b) The RDE plots of Ag/FNG under the laser-on/off conditions at a rotation rate of 1600 rpm. (c) The changes of hydrogen peroxide yield of various samples under cyclic laser-on/off conditions. (d) The proposed LORR enhancement at the Ag/ Fe_2O_3 interface.

LORR behaviors can be focused on the Ag/Fe₂O₃ heterojunction only by minimizing the potential interference that comes from other parts of the composites, such as graphene material excitation. The laser-coupled LSV curves of Ag/FNG (Fig. 4b) show similar onset potentials with a higher current density than the dark condition by 12.6%. The identical onset potentials suggest no change in the active site configuration, yet the quantity of catalytically reduced oxygen is increased under laser irradiation. Higher plateau currents in Ag/FNG reveal an increase in the oxygen molecule conversion equilibrium over time.

By comparing the difference of peroxide yields under laser-on/off conditions (Fig. 4c), the highly repeatable signals further indicate no potential decay of the photoactive sites due to laser irradiation. The laser-assisted peroxide inhibition of Ag/FNG, FNG, and Ag/N-rGO is shown to be 7.5%, 4.1%, and 2%, respectively. Moreover, the change in H₂O₂ yield of the heterojunction-free sample (Fig. S6, ESI†) is measured to be 4.0% which is comparable to that of FNG. The highest inhibition capability of Ag/FNG, which is even greater than the summation of bandgap excitation (FNG) and plasmonic resonance (Ag/N-rGO), as well as the noble metal alloys,⁹ reveals the strong photoelectrochemical interaction between Ag and Fe₂O₃ for peroxide depression. At the Ag/Fe₂O₃ heterojunction, the laser-excited hot electrons at the Ag nanoparticles can quickly transfer to the Fe₂O₃ conduction band with the lowered Schottky barrier, as illustrated in Fig. 4d.^{19,22} Together with the photoelectrons due to laser excitation on Fe₂O₃, the localization of these charges at the interfaces makes recombination less likely, to which the nearly four-electron reduction and further H₂O₂ inhibition can be attributed.⁹ It is also likely that the laser-activated Ag and Fe enhances the adsorption/desorption of oxygen simultaneously at the interface, which improves the mass transport and ORR kinetics for the increased plateau currents. To the best of our knowledge, Ag/FNG is the first LORR example achieving efficient kinetics and activities realized by the specific formation of Ag/Fe₂O₃ heterojunctions on graphene through the synthesis as demonstrated in this work.

In summary, we developed a two-step preparation to realize the formation of Ag/Fe₂O₃ heterojunctions on N-doped graphene, which has been experimentally confirmed as the origin of plateau currents and synergistic ORR enhancement achieving *n* values of 3.9 over a wide potential range with a minimized potential loss. N-doped graphene by DMF synthesis enhances the current density and lowers the onset potentials. Ag/FNG is capable of inhibiting peroxide yields under visible-light LORR, as a new example for the future design of a low-cost, photo-active composite to replace noble metal electrocatalysts. The detailed mechanisms regarding the photoelectrochemical ORR are currently under active investigation.

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Conflicts of interest

There are no conflicts to declare.

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