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## Silver nanostructure-loaded starch functionalized magnetite (Ag/s-Fe<sub>3</sub>O<sub>4</sub>) photocatalyst for H<sub>2</sub>O<sub>2</sub> production: experimental and molecular dynamics studies†

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The present research investigates photocatalytic H<sub>2</sub>O<sub>2</sub> formation on a composite of Ag and starch-stabilized Fe<sub>3</sub>O<sub>4</sub> (denoted as s-Fe<sub>3</sub>O<sub>4</sub>) nanoparticles. Starch functionalization of the Fe<sub>3</sub>O<sub>4</sub> part significantly improved the hydrophilicity of the composite. The charge carrier separation efficiency and photocatalytic activity changed with the amount of Ag loading on s-Fe<sub>3</sub>O<sub>4</sub>. H<sub>2</sub>O<sub>2</sub> production on this photocatalyst was investigated in pure water and aqueous solutions of various green sacrificial agents like glycerol. Classical molecular dynamics (MD) was employed to study the adsorption affinity of O<sub>2</sub> and H<sub>2</sub>O on the surface of Fe<sub>3</sub>O<sub>4</sub>, s-Fe<sub>3</sub>O<sub>4</sub>, and Ag/s-Fe<sub>3</sub>O<sub>4</sub> in an aqueous medium. MD results indicate that functionalizing Fe<sub>3</sub>O<sub>4</sub> with starch (s-Fe<sub>3</sub>O<sub>4</sub> system) enhances water adsorption affinity, and precipitating Ag nanostructures on s-Fe<sub>3</sub>O<sub>4</sub> (Ag/s-Fe<sub>3</sub>O<sub>4</sub>) increases O<sub>2</sub> adsorption affinity. Water contact angle measurements on Fe<sub>3</sub>O<sub>4</sub>, s-Fe<sub>3</sub>O<sub>4</sub>, and Ag/s-Fe<sub>3</sub>O<sub>4</sub> nanoparticles also quantify significantly better water adsorption due to starch functionalization. An aqueous solution of glycerol exhibited the best photocatalytic H<sub>2</sub>O<sub>2</sub> production activity. This result is critical given that glycerol is green, economical, and a byproduct of the biodiesel industry. A photocatalysis mechanism for H<sub>2</sub>O<sub>2</sub> generation on Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalysts has been proposed based on a series of control experiments and molecular dynamics simulations.

### 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), an essential green chemical, is utilized extensively in wastewater treatment (Fenton and photo-Fenton processes), organic synthesis, disinfection, pulp bleaching, and many other applications.<sup>1–3</sup> H<sub>2</sub>O<sub>2</sub> has also drawn interest as a potential substitute for H<sub>2</sub> as a fuel cell energy carrier in single-compartment cells for electricity production.<sup>4</sup> Such applications of H<sub>2</sub>O<sub>2</sub> have attracted the attention of different research groups to its production process.<sup>5</sup> Currently, the anthraquinone method is used for H<sub>2</sub>O<sub>2</sub> production at the industrial level. The method requires significant energy consumption due to multistep hydrogenation and oxidation reactions, along with the formation of several toxic by-products.<sup>6,7</sup>

Contrary to this, H<sub>2</sub>O<sub>2</sub> generation by photocatalysis is a low-cost and environmentally friendly process. It uses abundant and renewable resources like water, oxygen, and sunlight.<sup>4,8</sup> Photocatalytic H<sub>2</sub>O<sub>2</sub> production can occur either by a two-electron O<sub>2</sub> reduction pathway (O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub>O<sub>2</sub>) or a series of single-electron O<sub>2</sub> reductions (O<sub>2</sub> + e<sup>-</sup> → <sup>•</sup>O<sub>2</sub><sup>-</sup> followed by <sup>•</sup>O<sub>2</sub><sup>-</sup> + 2H<sup>+</sup> + e<sup>-</sup> → H<sub>2</sub>O<sub>2</sub>).<sup>9,10</sup> Most photocatalysts reported in literature generate H<sub>2</sub>O<sub>2</sub> from aqueous solutions of sacrificial agents, including methanol, ethanol, isopropanol, and oxalic acid.<sup>11,12</sup> Only a few photocatalysts have reported H<sub>2</sub>O<sub>2</sub> production from pure water.<sup>13,14</sup> In this context, green and economical sacrificial agents can also be used. Glycerol is a byproduct of biodiesel production, green and economical, but very few publications have investigated its efficacy as a sacrificial agent.<sup>15</sup>

A significant challenge for industrial applications of heterogeneous photocatalysts is their separation from the reaction system, recycling, and reuse. Superparamagnetic photocatalysts can be separated by magnetic decantation. After separation, the external magnetic field is removed, and photocatalyst nanoparticles can be re-dispersed in a separate solution by simply stirring.<sup>16,17</sup> In this context, fine Fe<sub>3</sub>O<sub>4</sub> nanoparticles are superparamagnetic, economical, and have visible

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range band gaps.<sup>18</sup> Nevertheless, bare Fe<sub>3</sub>O<sub>4</sub> nanoparticles suffer from poor water dispersibility. Fine Fe<sub>3</sub>O<sub>4</sub> nanoparticles, stabilized by various organic modifiers such as citrate and dextrin, exhibit energy band gaps exceeding 2.1 eV due to quantum size effects and enhanced water dispersibility.<sup>19,20</sup> Similarly, starch-stabilized magnetite nanoparticles display a comparable band gap and demonstrate excellent water dispersibility. Starch emerges as one of the potential functionalization agents in magnetite synthesis because it is green, abundant, and cost-effective. Starch contains many O–H functional groups, which can interact with and bind to the surface of nanoparticles during the initial nucleation stage.<sup>19,21</sup>

Adding a suitable noble metal cocatalyst (like Au, Ag, Pd, and Pt) to the primary semiconductor photocatalyst has been recommended to improve charge separation, O<sub>2</sub> adsorption, and its reduction.<sup>22–24</sup> For instance, H<sub>2</sub>O<sub>2</sub> formation increases when co-catalysts like Ag or Au nanostructures are attached to the semiconductor part.<sup>25,26</sup> Moreover, the nanoparticles of these noble metals efficiently absorb visible light of specific wavelengths owing to their localized surface plasmon resonance (LSPR) effect.<sup>27,28</sup> The re-emission of the absorbed energy in the visible range enhances the light absorption efficiency of the photocatalyst. The latter is an added advantage besides the cocatalyst properties. Moreover, the relatively lower cost of Ag nanoparticles favors their use as cocatalysts. Thus, Tsukamoto and colleagues reported the enhanced photocatalytic H<sub>2</sub>O<sub>2</sub> generation on the Ag/TiO<sub>2</sub> composite.<sup>26</sup> This improvement was attributed to the plasmonic Ag cocatalyst, which generates photoexcited electrons with favorable redox potentials capable of efficiently reducing oxygen.<sup>29</sup>

The current study investigates the photocatalytic H<sub>2</sub>O<sub>2</sub> production activity on Ag-loaded starch functionalized magnetite (abbreviated as Ag/s-Fe<sub>3</sub>O<sub>4</sub>) composite nanoparticles. Note that photocatalytic H<sub>2</sub>O<sub>2</sub> production on this composite has not been reported previously. The optical properties and band edges of the composite nanoparticles are thoroughly investigated. Their H<sub>2</sub>O<sub>2</sub> production photocatalytic activity is compared to pristine Fe<sub>3</sub>O<sub>4</sub> nanoparticles and Ag-loaded Fe<sub>3</sub>O<sub>4</sub> nanoparticles (without starch functionalization). Photogenerated charge transfer and separation are examined using photoluminescence (PL) and electrochemical analysis. X-ray photoelectron spectroscopy (XPS) analyzed the chemical species and their oxidation states on the composite surface. Large-scale classical molecular dynamics (MD) simulations investigated the adsorption affinity of O<sub>2</sub> and H<sub>2</sub>O molecules on the Fe<sub>3</sub>O<sub>4</sub>, s-Fe<sub>3</sub>O<sub>4</sub>, and Ag/s-Fe<sub>3</sub>O<sub>4</sub> systems. Several control experiments and MD simulations were conducted to obtain insight into the photocatalytic H<sub>2</sub>O<sub>2</sub> production mechanism.

## 2. Experimental section

### 2.1 Synthesis of starch-functionalized magnetite (s-Fe<sub>3</sub>O<sub>4</sub>)

A suitable volume of 0.4 M NaOH solution was heated at 80 °C. Then, an aqueous solution of FeSO<sub>4</sub>·7H<sub>2</sub>O (0.2M) and two wt% starch was added dropwise to it from the burette. The

temperature of the reaction mixture was maintained at 80 °C throughout this process, and the reaction was continued for 2 hours until the complete formation of a dark black precipitate. This precipitate was isolated *via* magnetic decantation and thoroughly washed multiple times with distilled water and ethanol until a neutral pH was achieved. Next, the washed precipitate was dried at 60 °C for 24 hours. This research publication uses the abbreviation s-Fe<sub>3</sub>O<sub>4</sub> (starch-functionalized magnetite) for these nanoparticles. A sample of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, without starch, was also prepared using a similar synthesis protocol.

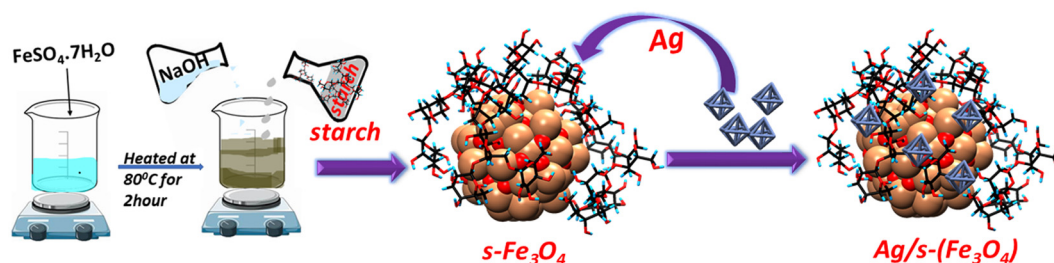
### 2.2 Synthesis of Ag-loaded s-Fe<sub>3</sub>O<sub>4</sub>

An appropriate amount of s-Fe<sub>3</sub>O<sub>4</sub> nanoparticles was dispersed in distilled water by bath sonication for 30 minutes. Next, a calculated amount of AgNO<sub>3</sub> (5, 10, and 20 wt%) solution was added to the dispersed solution of s-Fe<sub>3</sub>O<sub>4</sub>. The aqueous dispersion was agitated in a shaker for 12 hours. Then, 1 wt% starch and 0.1 M glucose were added to the mixture and heated at 60 °C for one hour. The pH of the mixture was maintained carefully at ~8 by adding an appropriate amount of 0.2 M NaOH solution. Next, the prepared composite was separated magnetically, and the product was washed multiple times with distilled water (DW) and ethanol. The product was subsequently dried for 20 hours at 50 °C. Samples prepared were coded as 5Ag/s-Fe<sub>3</sub>O<sub>4</sub>, 10Ag/s-Fe<sub>3</sub>O<sub>4</sub>, and 20Ag/s-Fe<sub>3</sub>O<sub>4</sub> based on the weight percent of AgNO<sub>3</sub> used in their preparation. Thus, 5, 10, and 20Ag represent the different weight percentages of silver loading on the s-Fe<sub>3</sub>O<sub>4</sub>. Additionally, one more sample, 10Ag/Fe<sub>3</sub>O<sub>4</sub>, was prepared using a protocol similar to the previous samples but without adding starch. It is labeled as 10Ag/Fe<sub>3</sub>O<sub>4</sub>, denoting ten-weight percent Ag loaded onto Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Scheme 1 illustrates the synthesis pathway for Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalysts.

### 2.3 Photocatalysis procedure

The photocatalyst sample (1 mg) was suspended in pure water or a sacrificial agent/water mixture (5/95%v/v; 12 ml) in a quartz tube. The tube was thoroughly sealed with a silicone rubber septum cap. Bath sonication was conducted for 10 minutes to ensure proper catalyst dispersion in the reaction mixture. Oxygen was bubbled into the suspension. Subsequently, the mixture was kept in the dark for 60 minutes to reach adsorption–desorption equilibrium. After that, the above-prepared mixture was photo-irradiated with visible light (cool white LED source; 1070 W m<sup>-2</sup>) for 60 minutes. The photocatalyst nanocomposite particles were quickly recovered from the suspension by magnetic separation. The H<sub>2</sub>O<sub>2</sub> production in the remaining aqueous solution was monitored by an iodometric method. H<sub>2</sub>O<sub>2</sub> molecules react with excess iodide anions (I<sup>-</sup>) under acidic conditions (H<sub>2</sub>O<sub>2</sub> + 3I<sup>-</sup> + 2H<sup>+</sup> → I<sub>3</sub><sup>-</sup> + 2H<sub>2</sub>O), producing triiodide anions (I<sub>3</sub><sup>-</sup>). The latter exhibits a significant absorption peak at approximately 350 nm. The quantity of I<sub>3</sub><sup>-</sup> was determined by interpolating the UV–visible absorbance at 350 nm in a standard H<sub>2</sub>O<sub>2</sub> calibration plot.<sup>10,30,31</sup> Separate photocatalytically produced H<sub>2</sub>O<sub>2</sub>





**Scheme 1** The synthesis pathway of Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalysts.

measurement experiments were performed under similar conditions with pure water, 5 vol% isopropanol, 5 vol% ethanol, and 5 vol% glycerol aqueous suspensions.

## 2.4 Computational studies

We employed the material and process simulation software (MAPS 4.01 by Scienomics) to construct the molecular models for MD simulations. In this research, three simulations were conducted to study the interaction of H<sub>2</sub>O<sub>2</sub> with Fe<sub>3</sub>O<sub>4</sub>, s-Fe<sub>3</sub>O<sub>4</sub>, and Ag/s-Fe<sub>3</sub>O<sub>4</sub> clusters. An initial supercell model was built using an inverse spinel FCC unit cell of Fe<sub>3</sub>O<sub>4</sub> (COD entry number: 907644). A nanocluster consisting of 149 atoms (Fe<sub>69</sub>O<sub>80</sub>) was constructed from the Fe<sub>3</sub>O<sub>4</sub> supercell, with the diameter of this Fe<sub>3</sub>O<sub>4</sub> nanocluster model measuring 1.4 nm. This Fe<sub>3</sub>O<sub>4</sub> nanocluster was then placed in the center of a cubic simulation box measuring 40 Å × 40 Å × 40 Å in dimensions (Fig. S1a†).

The first step for modeling s-Fe<sub>3</sub>O<sub>4</sub> was constructing an amylopectin unit composed of the C<sub>24</sub>H<sub>41</sub>O<sub>21</sub> molecular formula using the molecular builder plugin in MAPS software. The amylopectin unit was optimized by Modified Neglect of Diatomic Overlap (MNDO) using MAPS software. Then, five amylopectin units were positioned close to the above-constructed Fe<sub>3</sub>O<sub>4</sub> nanocluster (Fig. S1b†). After initial optimization, an MD equilibration run of ~1 ns was used to adsorb the amylopectin onto the magnetite nanocluster surface. The resulting model of the starch-functionalized Fe<sub>3</sub>O<sub>4</sub> nanocluster is named SFC. Similarly, the third model, Ag-loaded s-Fe<sub>3</sub>O<sub>4</sub>, was constructed. Initially, we carved a 0.6 nm Ag nanocluster with six atoms from an FCC Ag supercell. Subsequently, this Ag nanocluster was placed on the above-constructed s-Fe<sub>3</sub>O<sub>4</sub> model (Fig. S1c†).

H<sub>2</sub>O and O<sub>2</sub> molecules were constructed using the molecule builder plugin in MAPS and then optimized using the MNDO method. The H<sub>2</sub>O molecules were further modified with simple point charge (SPC) in Dreiding force field. The SPC charges for water molecules for Hydrogen and Oxygen are given in Table S1 (ESI†). This study inserted 20 O<sub>2</sub> and 2000 H<sub>2</sub>O molecules into the Fe<sub>3</sub>O<sub>4</sub>, s-Fe<sub>3</sub>O<sub>4</sub>, and Ag/s-Fe<sub>3</sub>O<sub>4</sub> cubic cluster systems, hereafter called FC, SFC, and AgSFC models. The insertions maintained a fixed density of approximately 1.05 g cc<sup>-1</sup>. Next, the conjugate gradient method was utilized to optimize the constructed simulation box. Following optimization, these models underwent MD simulations utilizing

MAPS's pre-installed LAMMPS (Large-scale Atomic Molecular Massively Parallel System) software. The MD simulations employed a modified 'Dreiding' force field. The potential energy contribution from non-bonded interactions in the 'Dreiding' force field was defined by the Lennard-Jones (LJ) 12-6 potential equation.<sup>32</sup>

$$E_{ij}^{LJ} = 4\epsilon_0 \left[ \left( \frac{\sigma_0}{r_{ij}} \right)^{12} - \left( \frac{\sigma_0}{r_{ij}} \right)^6 \right] \quad (1)$$

In eqn (1),  $\epsilon_0$  represents the potential well depth,  $\sigma_0$  is the van der Waals radii, and  $r_{ij}$  is the interatomic distance between atom types  $i$  and  $j$ .

Table S2† gives the L-J parameters used in this research. Periodic boundary conditions were applied across all dimensions of the simulation cell. The temperature was maintained at room temperature ( $T = 298.15$  K). MD simulations were conducted in the NVT ensemble over a ten-nanosecond (10 ns) period, employing a time step of one-femtosecond (1 fs). Coulomb interactions were computed using the particle mesh approach with a 12 Å cut-off distance.

## 3. Materials characterization

As-prepared photocatalysts' powder X-ray diffraction (XRD) patterns were captured on a Rigaku Miniflex 600 Desktop instrument (manufactured by RIGAKU Corporation). The device employed a Cu K $\alpha$  irradiation source (wavelength = 1.54 Å) with a scanning rate of 5° per minute and a step size of 0.01 while recording the patterns. A Tecnai G2 20 TWIN instrument (manufactured by EDAX Inc.) operating at an accelerating voltage of 200 kV was utilized for capturing transmission electron microscopy (TEM) images of different samples. The photocatalytic H<sub>2</sub>O<sub>2</sub> production was measured spectrophotometrically by an iodometric method using an Agilent Cary 60 UV-vis spectrophotometer instrument. Solid-state UV-vis reflectance spectroscopy was performed using a UV-2600 spectrophotometer (Shimadzu; Japan) from 200 to 1000 nm. XPS was conducted using an ESCA M-Probe instrument with an Al K $\alpha$  source. The photoluminescence (PL) spectra of the samples were captured using a Hitachi F-4600 spectrophotometer with an excitation wavelength of 280 nm. The prepared powder samples' magnetic characteristics were analyzed using a Microsense (EZ9) vibrating sample magnetometer (VSM).



## 4. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared  $s\text{-Fe}_3\text{O}_4$  and  $\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst. The characteristic diffraction pattern at scattering angles ( $2\theta$ ) of 18.33, 30.15, 35.51°, 37.15°, 43.2°, 53.56°, 57.12°, and 62.70° correspond to the  $\text{Fe}_3\text{O}_4$  with (111), (220), (311), (222) (400), (422), (511), and (440) crystal planes, respectively (JCPDS no. 88-0315). Two distinct sets of cubic Ag and  $\text{Fe}_3\text{O}_4$  diffraction peaks can be seen in the  $\text{Ag}/s\text{-Fe}_3\text{O}_4$  sample. The diffraction peaks of Ag nanoparticles at  $2\theta$  values of 38.12° and 44.39° can be attributed to the (111) and (200) crystallographic planes, which is consistent with the standard XRD data for the cubic (FCC) phase Ag (JCPDS no. 89-3722). This indicates the successful formation of metallic Ag-loaded  $\text{Fe}_3\text{O}_4$  nanoparticles.

Thermo-gravimetric analysis (TGA) was conducted on pure  $\text{Fe}_3\text{O}_4$  and  $s\text{-Fe}_3\text{O}_4$  samples to confirm the starch functionalization of  $\text{Fe}_3\text{O}_4$  nanoparticles. The TGA was carried out at a heating rate of 5 °C  $\text{min}^{-1}$  within 40 to 500 °C under a  $\text{N}_2$  atmosphere. Fig. S2† illustrates the TGA curves of the pure  $\text{Fe}_3\text{O}_4$  and  $s\text{-Fe}_3\text{O}_4$  samples. The pure  $\text{Fe}_3\text{O}_4$  nanoparticles displayed a weight loss of only 1.19 wt% due to the removal of adsorbed water molecules. In contrast, the TGA curve of the  $s\text{-Fe}_3\text{O}_4$  sample exhibited two distinct decomposition steps. The initial weight loss, occurring between 50–150 °C, was ascribed to starch dehydration, while the subsequent loss, observed from around 200 °C to 500 °C, corresponded to its

thermal decomposition. The starch content in  $s\text{-Fe}_3\text{O}_4$  was estimated to be 15.56% by weight.

Fig. 2 presents the TEM and HR-TEM images of pure  $\text{Fe}_3\text{O}_4$ ,  $s\text{-Fe}_3\text{O}_4$ , and 10 $\text{Ag}/s\text{-Fe}_3\text{O}_4$  nanoparticles. The TEM images reveal that pure  $\text{Fe}_3\text{O}_4$  and  $s\text{-Fe}_3\text{O}_4$  nanoparticles are mostly spherical (Fig. 2a and d). The HR-TEM image and inverse fast Fourier transform (IFFT) analysis of pure  $\text{Fe}_3\text{O}_4$  in Fig. 2(b and c) indicate a  $d$ -spacing of 0.48 nm, corresponding to the (111) crystal plane of  $\text{Fe}_3\text{O}_4$ . The average particle size for pure  $\text{Fe}_3\text{O}_4$  nanoparticles (Fig. 2a) is approximately 25–30 nm, while  $s\text{-Fe}_3\text{O}_4$  nanoparticles (Fig. 2d) have an average size of 10–12 nm. Thus, starch capping reduces the size of  $\text{Fe}_3\text{O}_4$  nanoparticles. Fig. 2e and f present the HRTEM image and IFFT analysis of the  $s\text{-Fe}_3\text{O}_4$  photocatalyst, revealing a lattice fringe of 0.48 nm, which confirms the successful synthesis of starch-functionalized  $\text{Fe}_3\text{O}_4$  nanoparticles.

Fig. 2g displays the TEM image of the 10 $\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst. The HR-TEM image and IFFT analysis of 10 $\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst in Fig. 2h and i display two adjacent regions with distinct lattice fringes 0.23 nm and 0.48 nm attributed to the (111) planes of Ag and the (111) planes of  $\text{Fe}_3\text{O}_4$ , indicating the formation of  $\text{Ag}/s\text{-Fe}_3\text{O}_4$  nanostructures. Additionally, Fig. S3a† presents the TEM images of the 20 $\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst, which clearly shows a morphology similar to that of 10 $\text{Ag}/s\text{-Fe}_3\text{O}_4$ . However, the increased Ag loading from 10 to 20 wt% results in noticeable agglomeration and dense Ag coverage. Fig. 2j shows the elemental mapping of the 10 $\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst. It reveals the homogeneous distribution of Fe, O, and Ag elements in a specific region within the SEM micrograph of the 10 $\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst sample. Furthermore, the Energy Dispersive X-ray Spectroscopy (EDS) data confirms that all elements (Fe, O, and Ag) are present in the sample in the expected stoichiometric proportions (Fig. S3b and c†).

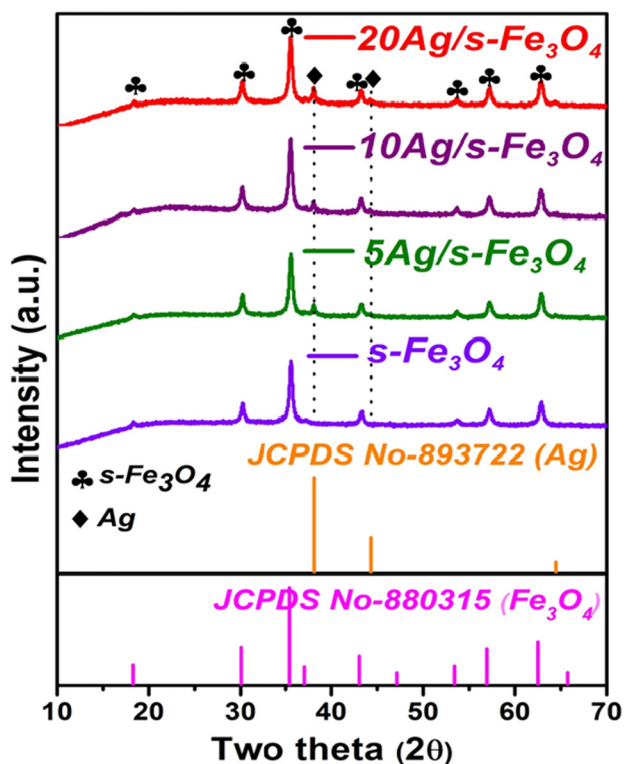


Fig. 1 XRD patterns of pure  $s\text{-Fe}_3\text{O}_4$  and different wt% of Ag-loaded  $s\text{-Fe}_3\text{O}_4$  photocatalysts.

### 4.1 Optical properties

The solid-state UV-visible absorption spectra of the as-prepared photocatalysts are depicted in Fig. 3a. It is observed that the absorption edge of the Ag-loaded  $s\text{-Fe}_3\text{O}_4$  samples falls within a similar range of visible wavelengths as the  $s\text{-Fe}_3\text{O}_4$  catalyst. The optical band gaps of  $\text{Fe}_3\text{O}_4$ ,  $s\text{-Fe}_3\text{O}_4$ , and Ag-loaded  $s\text{-Fe}_3\text{O}_4$  photocatalysts were determined from the Tauc plots (derived from the Kubelka–Munk equation).<sup>33,34</sup>

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2)$$

Here,  $\alpha$  represents the absorption coefficient,  $h$  represents Planck's constant,  $\nu$  is the light frequency,  $A$  denotes the proportionality constant, and  $E_g$  is the band-gap energy.

The Tauc plots (Fig. 3b) reveal that the band gaps of pure  $\text{Fe}_3\text{O}_4$ ,  $s\text{-Fe}_3\text{O}_4$ , and Ag-loaded  $\text{Fe}_3\text{O}_4$  (5, 10, 20 wt%) are 1.87, 2.28, and 2.28 eV, respectively. Moreover, it is observed that the band gap of  $\text{Fe}_3\text{O}_4$  (1.87 eV) is enhanced after functionalization with starch due to the smaller particle size (quantum size effect) of the  $s\text{-Fe}_3\text{O}_4$  sample (2.28 eV). Fig. 3c depicts the UV-visible absorbance spectra of aqueous sols of  $s\text{-Fe}_3\text{O}_4$ , 5 $\text{Ag}/s\text{-Fe}_3\text{O}_4$ ,



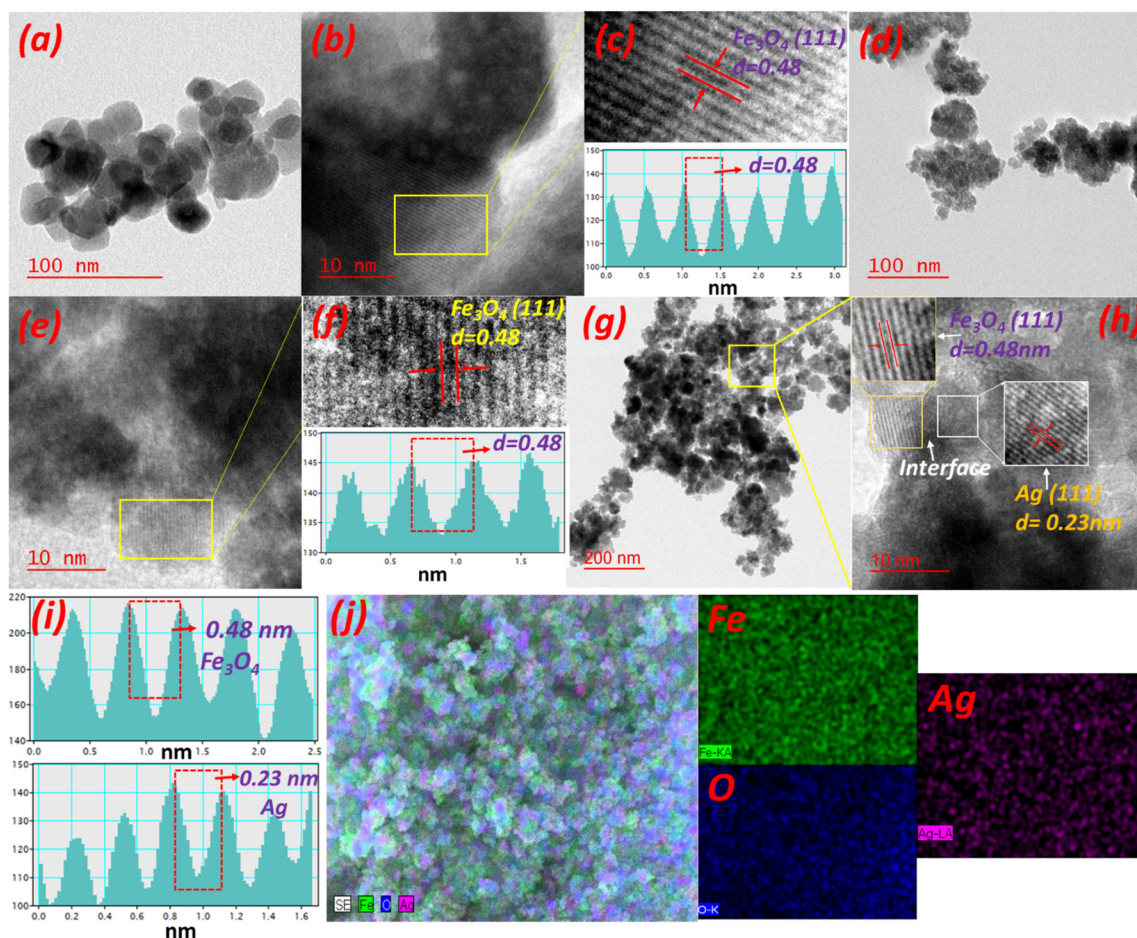


Fig. 2 TEM, HR-TEM, and IFFT analysis of (a–c) pure  $\text{Fe}_3\text{O}_4$  photocatalyst, (d–f)  $s\text{-Fe}_3\text{O}_4$  photocatalyst, and (g–i)  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst. (j) SEM images and corresponding elemental mapping of the  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst.

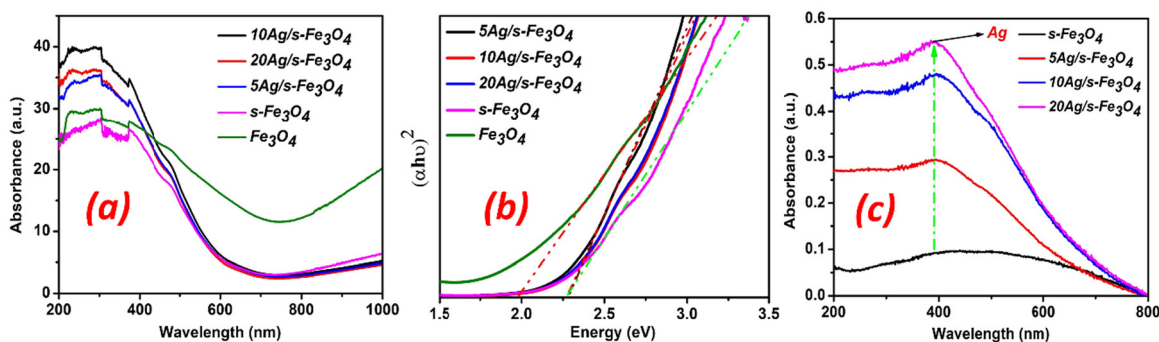


Fig. 3 (a) The solid-state UV absorbance spectra of the as-prepared photocatalyst, (b) the Tauc plot, and (c) the UV-visible absorbance spectra of aqueous sols of the nanoparticle samples.

$10\text{Ag}/s\text{-Fe}_3\text{O}_4$ , and  $20\text{Ag}/s\text{-Fe}_3\text{O}_4$  nanoparticles. Compared to the  $s\text{-Fe}_3\text{O}_4$  photocatalyst, Ag nanostructures loaded on the  $s\text{-Fe}_3\text{O}_4$  surface present stronger visible light absorption. The absorption peak at 395 nm corresponds to the LSPR absorbance of metallic Ag nanostructures on the  $\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalysts.

The PL spectra were acquired for  $s\text{-Fe}_3\text{O}_4$  and  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  using photoexcitation at 350 nm. As shown in Fig. S4a,† the PL

emission intensity decreases upon incorporating silver up to 10 wt% ( $10\text{Ag}/s\text{-Fe}_3\text{O}_4$ ). The lower PL emission intensity of the  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  sample compared to the  $s\text{-Fe}_3\text{O}_4$  photocatalyst suggests that it has the slowest electron–hole recombination, leading to higher photocatalytic capability.<sup>35</sup>

FTIR was employed to understand the interaction of starch and  $\text{Fe}_3\text{O}_4$  nanoparticles. Fig. S5 (ESI)† presents the FTIR



spectra of  $\text{Fe}_3\text{O}_4$  (without starch) and  $s\text{-Fe}_3\text{O}_4$  (starch functionalized) samples. In the FTIR spectrum of the  $s\text{-Fe}_3\text{O}_4$  sample, distinct peaks are observed at 2926, 1156, and 1032  $\text{cm}^{-1}$ , matching the stretching frequencies related to C–H, glycosidic C–O–C, and C–O bonds, respectively. As anticipated, these peaks are absent from the FTIR spectrum of the  $\text{Fe}_3\text{O}_4$  sample (before starch functionalization). The latter again confirms the successful preparation of starch-functionalized  $\text{Fe}_3\text{O}_4$  nanoparticles. The absorption peak at approximately 3430  $\text{cm}^{-1}$  is associated with vibrations corresponding to the stretching mode of O–H bonds. The signals at 1641  $\text{cm}^{-1}$  and 582  $\text{cm}^{-1}$  correspond to the hydroxyl groups on the surface of the  $\text{H}_2\text{O}$  molecule and Fe–O stretching vibrations.<sup>36,37</sup>

## 4.2 Electrochemical analysis

Fig. 4a presents the electrochemical impedance spectroscopy (EIS) of  $s\text{-Fe}_3\text{O}_4$  and different wt% of Ag-loaded  $s\text{-Fe}_3\text{O}_4$  photocatalysts, while the accompanying inset depicts the corresponding equivalent circuit model used for analysis. The parameters  $R_{ct}$  and  $R_s$  represent the charge transfer resistance and electrolyte solution resistance, within the equivalent circuit model, respectively. The Ag-loaded  $s\text{-Fe}_3\text{O}_4$  samples exhibit a smaller arc radius than pure  $s\text{-Fe}_3\text{O}_4$ , indicating reduced charge transfer resistance. Among all the photocatalysts, the 10Ag/ $s\text{-Fe}_3\text{O}_4$  sample demonstrates the smallest arc radius, demonstrating lower charge transfer resistance and superior charge separation in this composite.<sup>38</sup> This is consistent with this sample's enhanced photocatalytic performance and lowest PL intensity observations. Fig. S4b† illustrates the visible-light-induced photocurrent responses of the  $s\text{-Fe}_3\text{O}_4$ , 10Ag/ $s\text{-Fe}_3\text{O}_4$  samples for multiple on–off cycles. The significantly improved photocurrent density of 10Ag/ $s\text{-Fe}_3\text{O}_4$  under light exposure provided evidence for efficient charge carrier mobility resulting from the proper interface of the metallic Ag with  $s\text{-Fe}_3\text{O}_4$  photocatalyst. Additionally, the enhanced photocurrent density in the 10Ag/ $s\text{-Fe}_3\text{O}_4$  composite can be attributed to the effective suppression of recombination among photogenerated

charge carriers, which occurs due to the increased lifespan of excitons.<sup>38</sup>

The Mott–Schottky (MS) plots of the samples were analyzed to determine the semiconductor type and flat band potential of the synthesized photocatalysts.<sup>39</sup> These plots (Fig. 4b) exhibit positive slopes, showing that  $s\text{-Fe}_3\text{O}_4$  nanoparticles are n-type semiconductors. The  $x$ -axis intercept of the fits to the linear portions of these MS plots shows that the CB positions of  $s\text{-Fe}_3\text{O}_4$  nanoparticles are 0.28 V, respectively. The MS results are combined with the band gap values of  $s\text{-Fe}_3\text{O}_4$  (using the equation  $E_{CB} = E_{VB} - E_g$ ) to calculate respective VB positions.<sup>40</sup> Consequently, the VB positions are 2.56 V for  $s\text{-Fe}_3\text{O}_4$ . The following relationship is employed:  $V(\text{NHE}) = V(\text{Ag}/\text{AgCl}) + 0.059 \times \text{pH} + 0.197$  to convert potential measurements from the Ag/AgCl reference electrode scale to the NHE scale for all electrochemical assessments.<sup>41,42</sup>

The elemental compositions and surface electronic environment of the  $s\text{-Fe}_3\text{O}_4$  and 10Ag/ $s\text{-Fe}_3\text{O}_4$  photocatalysts were examined by XPS. Fig. S6† demonstrates the XPS survey spectra of the  $s\text{-Fe}_3\text{O}_4$  and 10Ag/ $s\text{-Fe}_3\text{O}_4$  samples, revealing the elemental composition of the prepared sample. This analysis confirms the presence of Fe, O, and C in  $s\text{-Fe}_3\text{O}_4$  and Fe, O, C, and Ag elements in the 10Ag/ $s\text{-Fe}_3\text{O}_4$  samples. Fig. 5(a–c) compares the high resolution (HR) XPS of Fe 2p and O 1s elements in pristine  $s\text{-Fe}_3\text{O}_4$  with the same species in 10Ag/ $s\text{-Fe}_3\text{O}_4$  sample. Fig. 5a shows the HR XPS of Fe 2p spectra for pristine  $s\text{-Fe}_3\text{O}_4$  and 10Ag/ $s\text{-Fe}_3\text{O}_4$  samples. Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> peaks at binding energies (BE) of 709.12 eV and 722.6 eV, respectively, in the  $s\text{-Fe}_3\text{O}_4$  sample, indicating the presence of Fe<sup>3+</sup> and Fe<sup>2+</sup> species. Furthermore, the presence of a satellite peak at 716.8 eV and 731.6 eV also suggests the coexistence of Fe<sup>2+</sup> and Fe<sup>3+</sup> (Fig. 5a).<sup>43</sup> The Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> peaks show a positive shift to 710.3 and 723.8 eV in the XPS of the 10Ag/ $s\text{-Fe}_3\text{O}_4$  sample (Fig. 5a). The HR XPS spectra of O 1s in pure  $s\text{-Fe}_3\text{O}_4$  and 10Ag/ $s\text{-Fe}_3\text{O}_4$  samples are shown in Fig. 5b. The three fitted distinctive peaks of O 1s at BE of 529.3, 531, and 532.2 are attributed to the Fe–O (lattice oxygen), hydroxyl, and

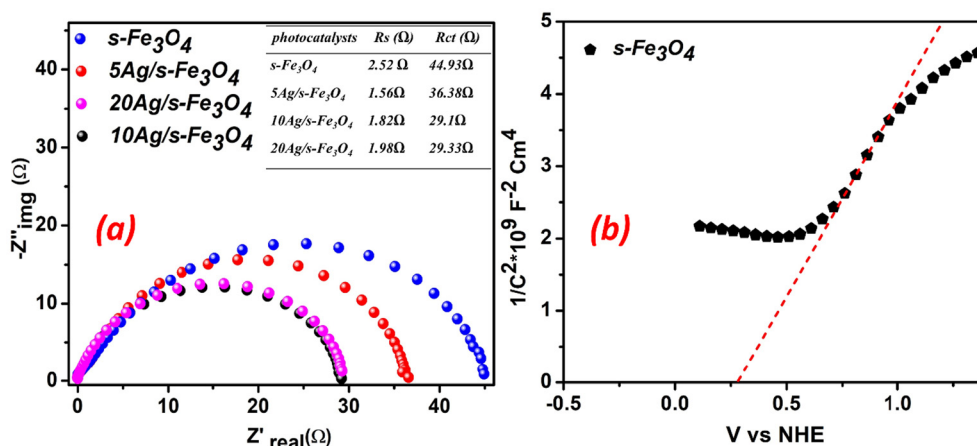


Fig. 4 (a) Nyquist plots of pure  $s\text{-Fe}_3\text{O}_4$  and different (wt% of) Ag-loaded  $s\text{-Fe}_3\text{O}_4$  photocatalysts and (b) Mott–Schottky plots for  $s\text{-Fe}_3\text{O}_4$  photocatalyst.



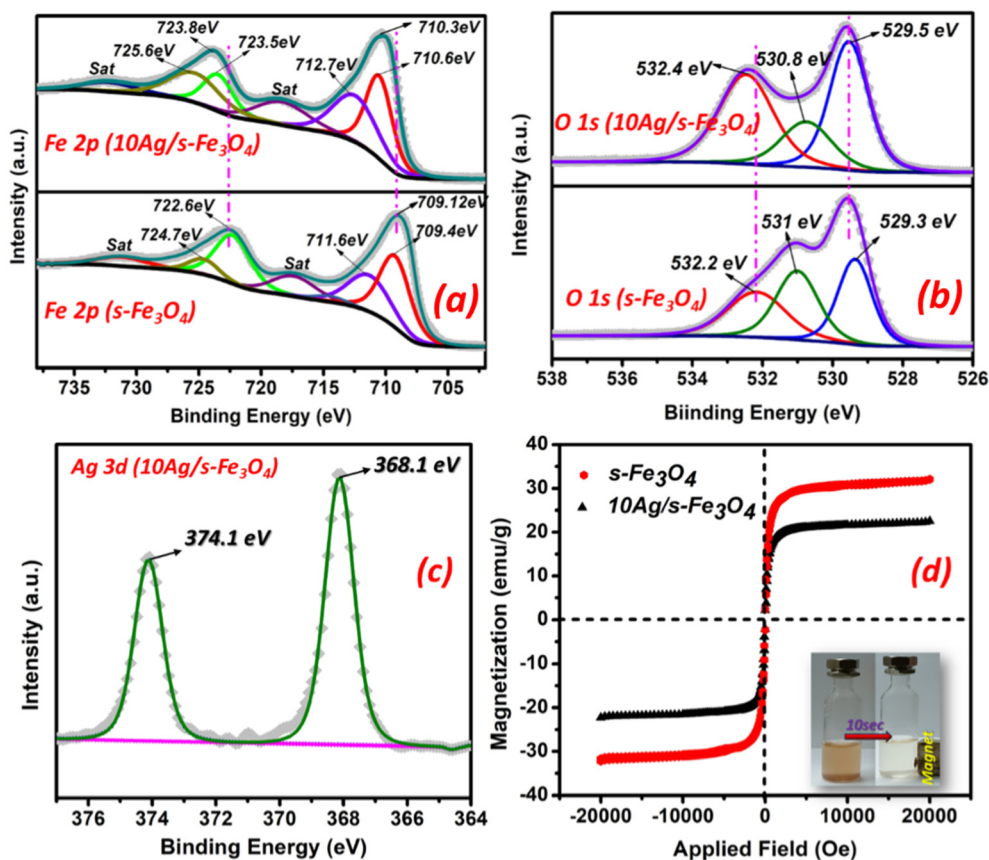


Fig. 5 XPS spectra of (a) Fe 2p of  $s\text{-Fe}_3\text{O}_4$  and  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$ , (b) O 1s of  $s\text{-Fe}_3\text{O}_4$  and  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$ , (c) Ag 3d of  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst. (d) Magnetization versus applied magnetic field plots of  $s\text{-Fe}_3\text{O}_4$  and  $\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalysts. The inset picture is of an aqueous dispersion of photocatalyst nanoparticles before and after magnetic separation.

surface adsorbed oxygen.<sup>44,45</sup> These peaks shift to 529.5, 530.8, and 532.4 eV in the  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  sample.

The Ag 3d spectrum in Fig. 5c displays two distinct peaks at 368.1 eV and 374.1 eV. These two peak locations correspond to the BE for Ag  $3d_{3/2}$  and Ag  $3d_{5/2}$ , respectively, which point to the presence of metallic silver ( $\text{Ag}^0$ ).<sup>46</sup> Additionally, the positive BE shift in the Fe 2p and O 1s peak positions in  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  compared to  $s\text{-Fe}_3\text{O}_4$  photocatalyst indicates charge transfer from  $s\text{-Fe}_3\text{O}_4$  nanoparticles to metallic Ag. It also demonstrates the chemical interaction between Ag metals and  $s\text{-Fe}_3\text{O}_4$  nanoparticles at the interface of the nanostructures.<sup>47,48</sup>

Fig. 5d shows the magnetization versus magnetic field ( $M\text{-}H$ ) curves of  $s\text{-Fe}_3\text{O}_4$  and  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst in the  $-20\text{ kOe} < H < +20\text{ kOe}$  range at room temperature (300 K). The photocatalysts  $s\text{-Fe}_3\text{O}_4$  and  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  demonstrated saturation magnetization ( $M_s$ ) values of 31.5 and 22.6  $\text{emu g}^{-1}$ , respectively. The S-shaped  $M\text{-}H$  curve with negligible hysteresis showed that the prepared nanoparticle samples were superparamagnetic.<sup>49,50</sup> These magnetic properties facilitate efficient magnetic separation of the photocatalyst when subjected to an external magnetic field. The inset image in the figure shows that the photocatalyst nanoparticles can be separated within 10 seconds using an external magnetic field.

### 4.3 MD results

Fig. 6(a–c) depicts the FC, SFC, and AgSFC system's snapshot at the end of a 10 ns equilibration run. The figures illustrate the distribution of  $\text{O}_2$  and  $\text{H}_2\text{O}$  molecules surrounding  $\text{Fe}_3\text{O}_4$ ,  $s\text{-Fe}_3\text{O}_4$ , and  $\text{Ag}/s\text{-Fe}_3\text{O}_4$  units. However, this depiction lacks quantitative insight into the probability of  $\text{O}_2$  and  $\text{H}_2\text{O}$  positions relative to the photocatalysts  $\text{Fe}_3\text{O}_4$ ,  $s\text{-Fe}_3\text{O}_4$ , and  $\text{Ag}/s\text{-Fe}_3\text{O}_4$  clusters. The snapshot of the  $\text{Ag}/s\text{-Fe}_3\text{O}_4$  model in Fig. 6c clearly shows the adsorption of  $\text{O}_2$  molecules on the Ag nanocluster (denoted by the green circle).

The intermolecular Radial Distribution Function (RDF) plots depicted in Fig. 7 elucidate the nature of interactions between different atom types comprising the FC, SFC, and AgSFC systems. RDF gives the atom type to atom type most probable distance. The RDF plots probe the molecular associations between iron (Fe) and oxygen (O) atoms in the  $\text{Fe}_3\text{O}_4$  nanocluster with atom types making  $\text{O}_2$  and  $\text{H}_2\text{O}$  molecules. Table 1 details the atom-type nomenclature used across all figures (Table 1) illustrating MD simulation results. The first interaction peak emerges at approximately 2.7 Å in the RDF of the FC. It demonstrates significant interaction between Fe atoms of  $\text{Fe}_3\text{O}_4$  and O atoms of  $\text{O}_2$  molecules. Another peak in



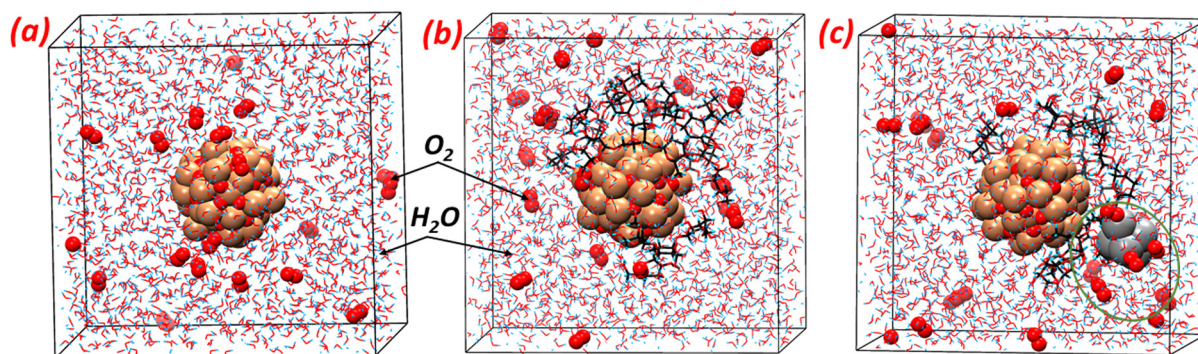


Fig. 6 shows a snapshot of the simulated system. (a) FC model (b) SFC model (c) AgSFC.

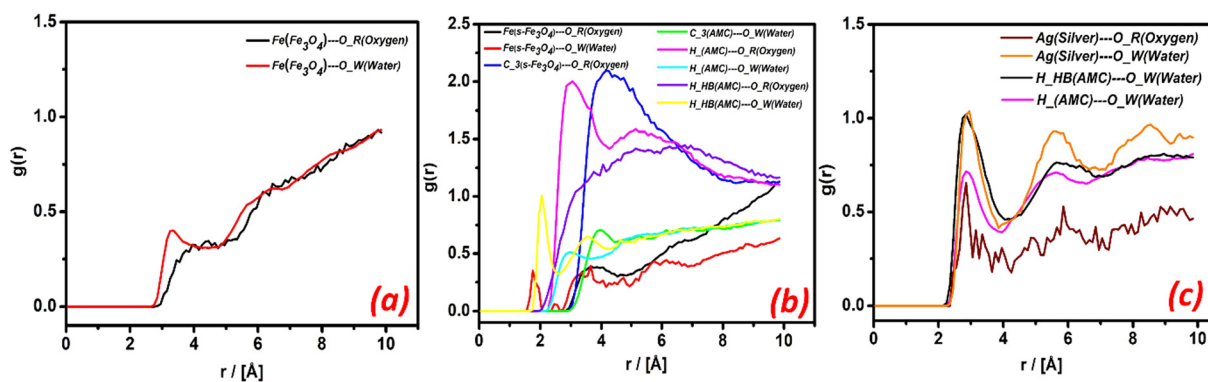


Fig. 7 RDF ( $g(r)$ ) vs. distance of interaction  $r/[\text{\AA}]$ . (a) FC model (b), SFC model (c), and AgSFC model.

Table 1 The naming convention used in the RDF plots is as follows

| Atom type | Meaning   |
|-----------|---|
| Fe        | The iron atom in $\text{Fe}_3\text{O}_4$                          |
| O_R       | Oxygen atom in the $\text{O}_2$ molecule                          |
| O_W       | Oxygen atom in the $\text{H}_2\text{O}$ molecule                  |
| Ag        | The silver atom of the Ag cluster                                 |
| H_HB      | Hydrogen atom is bonded to an oxygen atom in the amylopectin      |
| H_        | The hydrogen atom is bonded to the carbon atom in the amylopectin |
| C_3       | The carbon atom in amylopectin                                    |

Fig. 7a, which occurs at 2.9  $\text{\AA}$ , is between the Fe atoms of  $\text{Fe}_3\text{O}_4$  and the O atoms of  $\text{H}_2\text{O}$  molecules.

Fig. 7b shows the SFC (RDF) plots between atom types in s- $\text{Fe}_3\text{O}_4$  and those in  $\text{O}_2$  and  $\text{H}_2\text{O}$  molecules. Notably, amylopectin (AMC) molecules are partially adsorbed onto the  $\text{Fe}_3\text{O}_4$  nanocluster, leading to intermolecular interactions between AMC atom types (e.g., C and H) and the O atoms of both  $\text{O}_2$  and  $\text{H}_2\text{O}$  molecules. The H\_HB atoms of AMC in the s- $\text{Fe}_3\text{O}_4$  system display strong interaction peaks around 1.7  $\text{\AA}$  and 2.07  $\text{\AA}$  due to interactions between H\_HB $\cdots$ O\_W and H\_HB $\cdots$ O\_R. Similarly, two other peaks of H\_ atoms of AMC in the s- $\text{Fe}_3\text{O}_4$  system show interactions between H\_ $\cdots$ O\_R and

H\_ $\cdots$ O\_W at approximately 2.3  $\text{\AA}$ . The C\_3 atoms of AMC in the s- $\text{Fe}_3\text{O}_4$  system also show interactions with O\_W and O\_R at a similar peak distance of 3  $\text{\AA}$ . The Fe atoms of the s- $\text{Fe}_3\text{O}_4$  system display notable peak intensities for Fe $\cdots$ O\_W and Fe $\cdots$ O\_R at 1.56  $\text{\AA}$  and 2.9  $\text{\AA}$ , respectively.

Prominent peaks in the AgSFC systems (Fig. 7c) demonstrate that Ag has a strong interaction with the O\_R atom type in the 2.5 to 3  $\text{\AA}$  range. The Ag atom type also interacts with the O\_W atom type at a similar distance. At the same distance, there is also a strong interaction between the amylopectin H\_HB and the O\_W atom types. Furthermore, Fig. S7 in the ESI $^\dagger$  illustrates the atom-type interactions in the AgSFC model, specifically between Fe and O\_W, as well as between C\_3 (AMC) and both O\_R and O\_W. Thus, functionalizing  $\text{Fe}_3\text{O}_4$  with starch (SFC system) enhances water adsorption affinity, and incorporating Ag onto s- $\text{Fe}_3\text{O}_4$  (AgSFC system) increases  $\text{O}_2$  adsorption affinity.

#### 4.4 Photocatalytic $\text{H}_2\text{O}_2$ production activity

No  $\text{H}_2\text{O}_2$  production was detected on the prepared photocatalysts under dark conditions. Subsequently, all samples' photocatalytic activities for  $\text{H}_2\text{O}_2$  production were evaluated under visible light irradiation using only water at neutral pH. The pristine  $\text{Fe}_3\text{O}_4$  and s- $\text{Fe}_3\text{O}_4$  (without silver loading) nanoparticles showed inefficient  $\text{H}_2\text{O}_2$  production due to poor



visible light absorption and quick photoinduced charge carrier recombination. A considerable amount of  $\text{H}_2\text{O}_2$  formation was detected from pure water following 60 minutes of visible light exposure at a neutral pH on Ag-loaded  $s\text{-Fe}_3\text{O}_4$  nanostructures. The  $\text{H}_2\text{O}_2$  production on  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  was calculated to be  $167 \mu\text{mol g}^{-1} \text{h}^{-1}$  and  $\sim 16$  times higher than that of  $s\text{-Fe}_3\text{O}_4$ . The 10 wt% Ag loading on the  $s\text{-Fe}_3\text{O}_4$  nanostructure photocatalyst exhibits optimal photocatalytic  $\text{H}_2\text{O}_2$  production activity at 60 min light exposure. However, when the Ag nanoparticle loading on  $s\text{-Fe}_3\text{O}_4$  exceeds 10 wt%, the  $\text{H}_2\text{O}_2$  formation rate decreases to  $157 \mu\text{mol g}^{-1}$ . This reduction is attributed to agglomeration and excessive surface coverage at higher Ag loading (20 wt%), which can block active sites, hinder light penetration, and introduce recombination centers, ultimately reducing the photocatalytic activity. This is supported by the TEM image of the  $20\text{Ag}/s\text{-Fe}_3\text{O}_4$  sample (Fig. S3a, ESI<sup>†</sup>), which clearly shows agglomeration and dense Ag coverage. Fig. 9a indicates that the  $10\text{Ag}/\text{Fe}_3\text{O}_4$  photocatalyst, without starch functionalization, also exhibited an  $\text{H}_2\text{O}_2$  generation rate of  $83 \mu\text{mol g}^{-1} \text{h}^{-1}$ . This value is almost half the  $\text{H}_2\text{O}_2$  generation rate observed for the  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  (starch functionalized) photocatalyst. This comparison suggests that the starch-functionalized Ag-loaded  $\text{Fe}_3\text{O}_4$  ( $10\text{Ag}/s\text{-Fe}_3\text{O}_4$ ) photocatalyst significantly enhances its photocatalytic activity for  $\text{H}_2\text{O}_2$  production. Starch functionalization on  $\text{Fe}_3\text{O}_4$  makes its surface considerably more hydrophilic, demonstrating strong water adsorption. The increase in photocatalyst surface hydrophilicity likely improves the water oxidation efficiency, resulting in a higher  $\text{H}_2\text{O}_2$  generation rate.

To explore the surface properties of the synthesized  $\text{Fe}_3\text{O}_4$ ,  $s\text{-Fe}_3\text{O}_4$ , and  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalysts, the water contact angle (WCA) was measured on a pellet of each photocatalyst (Fig. 8). A decrease in the WCA indicates strong material adsorption (hydrophilicity). Pure  $\text{Fe}_3\text{O}_4$  (without starch) displays a contact angle of  $52.95^\circ$ , highlighting its poor water adsorption (hydrophobic) nature (Fig. 8a). Following the functionalization with starch and Ag loading on  $\text{Fe}_3\text{O}_4$ , the resulting photocatalysts,  $s\text{-Fe}_3\text{O}_4$  and  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$ , exhibit calculated contact angles of  $26^\circ$  and  $25.2^\circ$ , respectively, indicating an enhancement in hydrophilic properties (Fig. 8b and c). These findings demonstrate that the improved hydrophilicity

of  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  promotes more efficient water oxidation. This also leads to longer residence times for solvent molecules, improving their interaction with photocatalyst particles and reactants.<sup>51</sup>

The photocatalytic experiments were conducted under four different pH conditions (pH 2, 3, 5, and 7) to investigate the influence of pH on  $\text{H}_2\text{O}_2$  generation. The results revealed that the photocatalytic  $\text{H}_2\text{O}_2$  production was significantly affected by the pH of the aqueous solution. Fig. 9b shows that  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  exhibited the highest photocatalytic activity for  $\text{H}_2\text{O}_2$  production at pH 3 ( $258.7 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) compared to the other three pH values. This observation suggests that excess protons at pH 2 might gradually oxidize the produced  $\text{H}_2\text{O}_2$  into  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$ ). Conversely, in a less proton-rich environment at pH 5 and 7, the  $\text{H}_2\text{O}_2$  production was lower due to faster  $\text{H}_2\text{O}_2$  decomposition.<sup>30</sup> Consequently, a pH value of 3 was optimal for photocatalytic  $\text{H}_2\text{O}_2$  production.

To gain more insight, additional controlled experiments were conducted to investigate how different gas environments (air,  $\text{O}_2$ , and  $\text{N}_2$ ) affect the photocatalytic activity of the  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst in  $\text{H}_2\text{O}_2$  production (Fig. 9c). The findings indicate that substituting  $\text{O}_2$  with  $\text{N}_2$  leads to a notable inhibition of the photocatalytic efficiency in the ORR, emphasizing the crucial role of dissolved  $\text{O}_2$  during the ORR to  $\text{H}_2\text{O}_2$  production process. To compare the results, photocatalytic tests were also conducted with different sacrificial agents (ethanol, IPA, and glycerol) on  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalyst to determine whether these electron donor molecules could speed up the formation of  $\text{H}_2\text{O}_2$ . Adding 5-vol% glycerol in water enhances ( $\sim 2.5$  times) the formation of  $\text{H}_2\text{O}_2$  compared to pure water at pH 3. Fig. 9d compares the photocatalytic  $\text{H}_2\text{O}_2$  formation activity on a  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  sample with different sacrificial agents after 60 minutes of visible light irradiation. Additionally, Fig. 9h compares the results of photocatalytic  $\text{H}_2\text{O}_2$  production of  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  with other reported photocatalysts under different sacrificial agents in recent years. The detailed information on the previously reported photocatalysts is mentioned in Table S3 (ESI<sup>†</sup>).

The photocatalytic  $\text{H}_2\text{O}_2$  formation experiment was repeated eight times to examine the long-term stability of

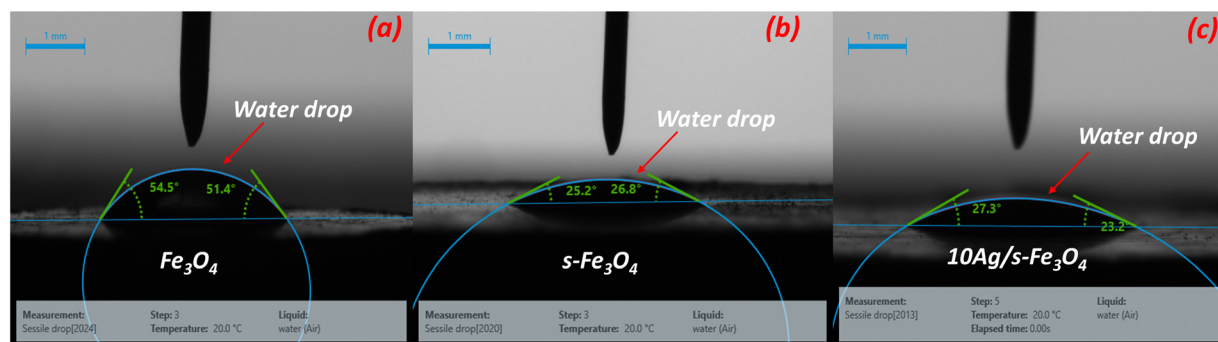
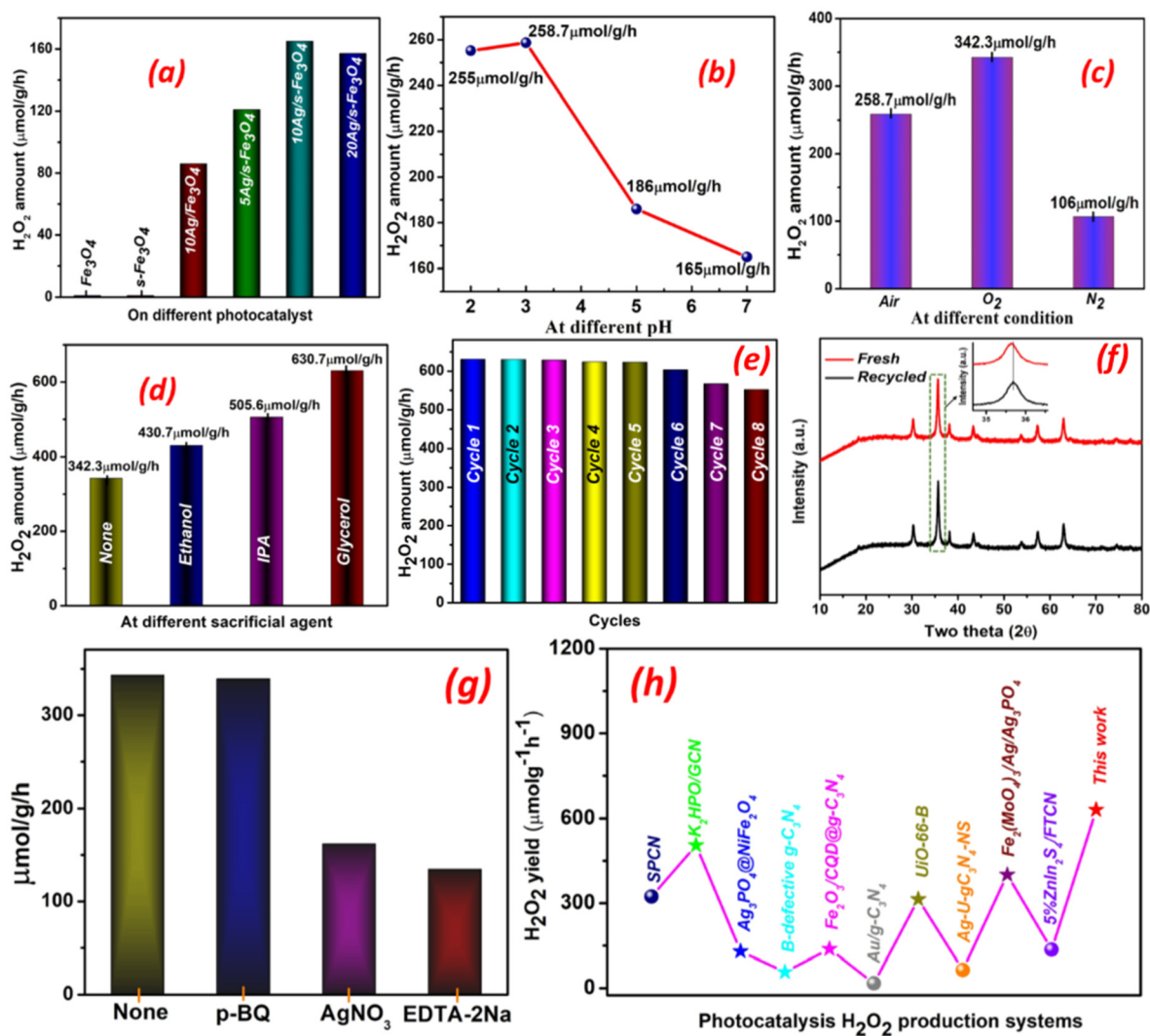


Fig. 8 Contact angle measurement on (a)  $\text{Fe}_3\text{O}_4$ , (b)  $s\text{-Fe}_3\text{O}_4$ , and (c)  $10\text{Ag}/s\text{-Fe}_3\text{O}_4$  photocatalysts.





**Fig. 9** (a) H<sub>2</sub>O<sub>2</sub> production on different samples from pure water at neutral pH (b) H<sub>2</sub>O<sub>2</sub> production at different pH on 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst (c) H<sub>2</sub>O<sub>2</sub> production at different conditions on 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst (d) H<sub>2</sub>O<sub>2</sub> production using different sacrificial agents on 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst (e) recyclability performance on 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst (f) XRD of recycled photocatalyst (10Ag/s-Fe<sub>3</sub>O<sub>4</sub>) (g) effect of different trapping agent on photocatalytic H<sub>2</sub>O<sub>2</sub> production on 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst (h) comparison data for photocatalytic H<sub>2</sub>O<sub>2</sub> production with other previously reported photocatalysts in recent works.

the 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> catalyst further. After each cycle, the photocatalyst was rinsed with distilled water and subsequently separated from the solution *via* magnetic decantation. The recovered sample was then reused for the next reaction cycle. The recyclability results show that the photocatalytic performance remains stable, with around a 13% reduction observed after the 8th cycle, indicating good long-term durability of the photocatalyst, as shown in Fig. 9e. Additionally, to evaluate the stability of the 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst after photocatalytic cycles, XRD, TEM, and UV-visible spectroscopy analyses were performed on the recycled sample. The XRD pattern (Fig. 9f) shows no significant changes, indicating that the crystal structure remains largely intact. A very minor shift in the diffraction peaks was observed, which can be attributed to surface

oxygen passivation. TEM analysis (Fig. S8a†) was conducted to assess any morphological changes after recycling. The images confirm that the photocatalyst retains its structural integrity, with no noticeable aggregation of Ag nanoparticles, demonstrating good morphological stability. Furthermore, UV-Visible absorption spectra of the fresh and recycled samples (Fig. S8b†) show that the characteristic plasmonic peak of Ag nanoparticles, typically observed around 395 nm, remains unchanged after repeated photocatalytic cycles. This stable plasmonic response suggests negligible Ag leaching during the reaction. These results collectively confirm that the 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst exhibits excellent structural and photochemical stability, making it highly suitable for efficient and repeated H<sub>2</sub>O<sub>2</sub> generation under photocatalytic conditions.



## 5. Photocatalytic H<sub>2</sub>O<sub>2</sub> production mechanism

The schematic in Fig. 10 proposes a possible photocatalytic H<sub>2</sub>O<sub>2</sub> formation on the Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst. The series of experiments and MD simulation results facilitated the development of this mechanism. The experimental results show that photocatalytic H<sub>2</sub>O<sub>2</sub> production activity increases substantially on the 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst compared to pristine and different Ag-loaded s-Fe<sub>3</sub>O<sub>4</sub>. The EIS, PL, and photocurrent results indicate that charge separation on the 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalyst reduces the likelihood of charge carrier recombination.

Active species trapping experiments were conducted using *p*-benzoquinone (PBQ), AgNO<sub>3</sub>, and ethylenediamine tetraacetic acid disodium (EDTA-2Na) as scavengers for superoxide radicals (<sup>•</sup>O<sub>2</sub><sup>-</sup>), electrons (e<sup>-</sup>), and a hole scavenger, respectively. As shown in Fig. 9g, there is a significant decrease in H<sub>2</sub>O<sub>2</sub> yield when AgNO<sub>3</sub> and EDTA-2Na are employed as scavenger agents, which means that e<sup>-</sup> and h<sup>+</sup> play a crucial role in the oxygen reduction and water oxidation reaction. The performance of H<sub>2</sub>O<sub>2</sub> production remains unaffected by the addition of PBQ, indicating superoxide radicals are not the active species for photocatalytic H<sub>2</sub>O<sub>2</sub> generation. The formation of the <sup>•</sup>O<sub>2</sub><sup>-</sup> in the photocatalytic reaction is further examined by the nitro blue tetrazolium test (NBT). Fig. S9† depicts the absorption peak intensity of the NBT solution at 262 nm. Following the photocatalytic reaction, no alterations were noted in the absorption peak of the NBT solution, confirming that <sup>•</sup>O<sub>2</sub><sup>-</sup> does not serve as an active species in reducing O<sub>2</sub> to produce H<sub>2</sub>O<sub>2</sub>.

The photocatalytic activity is directly affected by the effective adsorption of reactants, particularly water and oxygen. Therefore, it is vital to consider H<sub>2</sub>O and O<sub>2</sub> adsorption on the photocatalyst surface in aqueous conditions. As

illustrated by the MD simulation results, water adsorption predominantly takes place on the s-Fe<sub>3</sub>O<sub>4</sub> surface, and oxygen adsorption takes place on the Ag of the Ag/s-Fe<sub>3</sub>O<sub>4</sub> nanostructure. Starch functionalization of the Fe<sub>3</sub>O<sub>4</sub> improves its hydrophilicity, which is necessary for efficient water oxidation. WCA measurements show that the 10Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalytic system has maximum water adsorption affinity.

The visible light illumination of the Ag/s-Fe<sub>3</sub>O<sub>4</sub> photocatalysts photo-excited electrons from the VB of the s-Fe<sub>3</sub>O<sub>4</sub> component. The H<sub>2</sub>O molecules got oxidized by photo-generated holes in the VB of the photocatalyst and generated the H<sup>+</sup> and O<sub>2</sub>. Note that the VB position of s-Fe<sub>3</sub>O<sub>4</sub> is 2.56 V vs. NHE, providing sufficient overpotential for water oxidation (1.23 V vs. NHE). H<sub>2</sub>O<sub>2</sub> concentrations of 258.7 μmol g<sup>-1</sup> h<sup>-1</sup> and 106 μmol g<sup>-1</sup> h<sup>-1</sup> were maintained without an external O<sub>2</sub> supply. This observation indicates that O<sub>2</sub> is generated through water oxidation. Moreover, adding a suitable sacrificial agent (such as ethanol, IPA, or glycerol) significantly boosts H<sub>2</sub>O<sub>2</sub> production by promoting its activation. This enhancement occurs as photogenerated holes are effectively scavenged through the oxidation of the sacrificial agent. Additionally, this process generates H<sup>+</sup> ions, which subsequently react with adsorbed O<sub>2</sub> via the 2e<sup>-</sup> ORR to produce H<sub>2</sub>O<sub>2</sub> (O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub>O<sub>2</sub>).

## 6. Conclusions

An efficient, visible-light-driven, and magnetically recyclable photocatalyst (Ag/s-Fe<sub>3</sub>O<sub>4</sub>) for H<sub>2</sub>O<sub>2</sub> production was successfully synthesized using a two-step precipitation method. Fine Ag nanostructures were deposited on starch-functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticle surfaces, where starch functionalization played a crucial role in preventing nanoparticle aggregation and reducing their size. Furthermore, water contact angle (WCA) measurements confirmed that starch functionalization enhances water wettability, making the photocatalyst surface more hydrophilic. MD simulations revealed that Ag loading on s-Fe<sub>3</sub>O<sub>4</sub> enhances O<sub>2</sub> adsorption, while starch improves water molecule adsorption. The increased O<sub>2</sub> adsorption on Ag nanostructures is well known for facilitating oxygen reduction via the two-electron pathway, leading to efficient H<sub>2</sub>O<sub>2</sub> production. Additionally, scavenger experiments confirmed that photocatalytic H<sub>2</sub>O<sub>2</sub> production over Ag/s-Fe<sub>3</sub>O<sub>4</sub> occurs through the two-electron O<sub>2</sub> reduction pathway. The Ag loading on s-Fe<sub>3</sub>O<sub>4</sub> was optimized, with 10 wt% Ag deposition exhibiting the highest photocatalytic H<sub>2</sub>O<sub>2</sub> production activity. However, excessive Ag deposition (20 wt%) reduced photocatalytic performance by covering the active sites on the s-Fe<sub>3</sub>O<sub>4</sub> surface, while 5 wt% Ag loading resulted in poor charge transfer efficiency. The combined experimental and molecular dynamics study provides valuable insights for designing efficient photocatalysts for H<sub>2</sub>O<sub>2</sub> production via the two-electron O<sub>2</sub> reduction pathway. This investigation highlights the significance of concurrent water adsorption on the

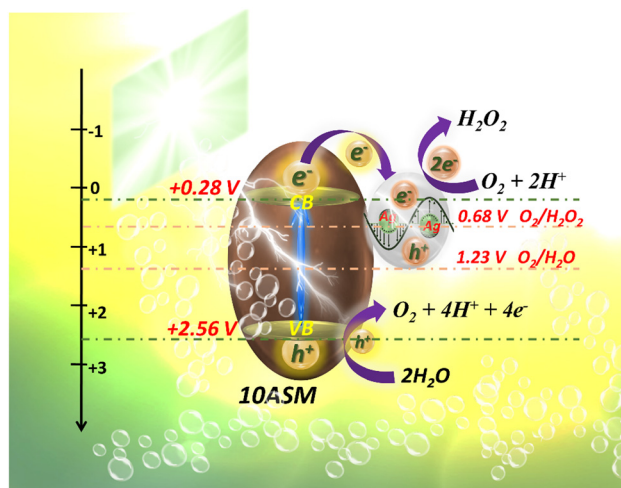


Fig. 10 Proposed mechanism for photocatalytic H<sub>2</sub>O<sub>2</sub> production on 10Ag/s-Fe<sub>3</sub>O<sub>4</sub>.



VB part and oxygen interaction with the CB part of the photocatalyst for designing effective H<sub>2</sub>O<sub>2</sub>-producing photocatalysts.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Data are available upon request from the authors.

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