Fabrication of pristine Mn$_2$O$_3$ and Ag–Mn$_2$O$_3$ composite thin films by AACVD for photoelectrochemical water splitting†

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Pristine Mn$_2$O$_3$ and Ag–Mn$_2$O$_3$ composite thin films have been developed on fluorine doped tin oxide (FTO) coated glass substrates at 450 °C by aerosol assisted chemical vapor deposition (AACVD) using a methanol solution of a 1:2 mixture of acetatoargentate(Ⅰ). Ag(CH$_3$COO), and a newly synthesized manganese complex, [Mn(dmae)$_2$(TFA)$_4$] (1) (dmae = N,N-dimethylaminoethanolate, TFA = trifluoroacetate). The phase purity and stoichiometric composition of the films were investigated by X-ray diffraction (XRD) and Raman spectroscopy techniques. Energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS) analyses revealed a Ag to Mn ratio of 1:2 and further confirmed the uniform dispersion of Ag nanoparticles into the Mn$_2$O$_3$ structure. Optical studies showed a direct band gap of 2.6 eV for the pristine Mn$_2$O$_3$ film that was lowered to 1.8 eV for Ag–Mn$_2$O$_3$ due to the plasmonic interaction of Ag with Mn$_2$O$_3$. The Ag–Mn$_2$O$_3$ composite film displayed enhanced photocatalytic activity in photoelectrochemical (PEC) water splitting and yielded a photocurrent of 3 mA cm$^{-2}$ at 0.7 V versus Ag/AgCl which was 1.6 times higher than a pristine Mn$_2$O$_3$ film alone, under AM 1.5 G illumination (100 mW cm$^{-2}$). The high PEC efficiency is mainly due to the plasmonic effect of Ag nanoparticles, which enhances the visible light absorption, efficient electron–hole separation and high carrier mobility of the Ag–Mn$_2$O$_3$ photoelectrode. The charge carrier density of Ag–Mn$_2$O$_3$ is two times higher than the pristine Mn$_2$O$_3$ as calculated by the Mott–Schottky plot. Based on the PEC studies a mechanism is proposed to elucidate the high activity of Ag–Mn$_2$O$_3$ in PEC water splitting.

1. Introduction

Photoelectrochemical (PEC) water splitting to produce hydrogen and its use as a cheap and clean fuel is an efficient and promising way to solve future energy and environmental challenges. To accomplish this photoelectrolysis, an economically viable water splitting cell, composed of stable semiconductors designed to split water directly on the semiconductor surface, needs to be developed. A variety of photoactive materials have been designed and developed with the aim to fix the main PEC obstacles such as the appropriate conduction/valence band position, narrowing of the band gap to harness visible light, and fast electron/hole pair separation/transportation. However, these extensive studies could not find an individual material which could overcome all these issues at once. The main criteria for a photocatalyst material include low cost, environmentally friendly nature, high efficiency and stability under visible light irradiation. TiO$_2$ is a strong candidate due to its high stability in aqueous solutions and high photocatalytic activities but its efficiency is restricted to working under UV light due to its limitation of a large band gap of 3–3.2 eV. Among the different semiconducting materials, manganese based oxides can be advantageous instead of TiO$_2$ for photocatalytic applications because of their low cost, high abundance, chemical and structural stabilities and the ability to show multiple oxidations states (MnO$_2$, Mn$_3$O$_4$, Mn$_2$O$_3$, etc.). Recent determination of the structure of photosystem II revealed that a co-ordinated cluster Mn$_4$CaO$_5$ under a well-defined protein environment is responsible for the photooxidation of water in plant cells. The manga-
nese atom in this complex exists in variable valences of (iii) and (iv).17–19 These studies indicate the importance of manganesene in photocatalytic systems and also show that a highly efficient optoelectronic and photocatalytically active device similar to that of plants requires a high degree of dispersion of the common metals in the oxide systems.

We have investigated several manganese oxide based photocatalysts such as Mn(OH)2–TiO2,20 Mn2O3–TiO2,21 MnO2–CeO2,22 and solid solution of MnZnO3,23 and found them advantageous for PEC water splitting applications. These studies revealed that the coupling of two semiconductors might result in improved interfacial charge transfer thereby minimizing charge recombination, lowering the band gap and ultimately boosting photo-activity in the visible region. Single phase MnZnO3 due to its distorted and charged layer ilmenite structure, exhibited good optoelectronic properties for photocatalytic applications.

Recent investigations have established that incorporation of plasmonic metal nanoparticles into a semiconductor is an effective strategy to enhance solar-light harvesting and the energy-conversion efficiency.24,25 When PEC water splitting is carried out with plasmonic metal integrated metal oxides, the hot electron of the noble metal is injected into the conduction bands of metal oxides which increases the power absorbed in this region and enhances the efficiencies of the devices by preventing the electron hole recombination.26–28 Among all noble metals, silver is mostly employed in photocatalysts because of its abundancy, much lower cost and non-toxicity compared to noble metals such as Au, Pd and Pt.29–31 The linkage of Mn2O3 with Ag is a promising strategy for photocatalytic hydrogen production under visible light irradiation because Ag can markedly facilitate the separation of electrons and holes at the interface and improve the transfer efficiency of photocarriers. In addition, Ag has a surface plasmon resonance (SPR) effect to enhance visible-light absorption ranging from 400 to 800 nm.32,33 Only a few reports on the synthesis of silver–manganeseoxide nano-composites are found in the literature. Yu Lei et al. prepared Ag–Mn2O3 nanofibers by a facile two-step procedure (electro-spinning and calcination) and employed them as an immobilization matrix for glucose oxidase to construct an amperometric glucose biosensor.34 In another report, novel hierarchical flower-like nanostructures of Ag–MnO2 were achieved by facile wet chemical and photochemical routes.35 However, to the best of our knowledge, Ag–Mn2O3 nanostructured enhanced PEC water splitting has not been investigated so far.

Recently several plasmonic photocatalytic systems such as Au/Pt/g-C3N4,36 Au/ZnO,37 Ag/CuO,38 Au/TiO2,39 Au/TiO2 nanotube arrays40 have been studied for the enhancement of renewable hydrogen evolution through photocatalytic water splitting. Hence, this strategy provides new opportunities to develop unique types of photoelectrodes to enhance PEC water splitting.

In the present work we report fabrication of manganese(n) oxide (Mn2O3) and 1:2 Ag–Mn2O3 composite thin films on FTO for enhanced visible light absorption, efficient e−–h+ separation and high carrier mobility of the Ag–Mn2O3 photoelectrode. A comparison of PEC properties of Mn2O3 and the Ag–Mn2O3 composite indicates that the latter is 1.6 times more efficient than the former. The AACVD is considered to be the most versatile technique for making multicomponent photoelectrodes in a single step with potential values of exact stoichiometry, controlled homogeneity, better uniformity and attractive nanostructures which is sometimes unachievable via conventional synthetic methods.40–42 However, these advantages can only be achieved by using an appropriate choice of precursors. Therefore, we synthesized a specifically tailored oxygen rich complex Mn(dmae)[TFA]4 (1) and implemented it as a precursor for the formation of pristine Mn2O3 thin films on FTO glass substrates at 450 °C. The deposition of Ag–Mn2O3 nanocomposite thin films was achieved by using a homogeneous solution of precursor (1) and Ag(CH3COO) at 450 °C under AACVD conditions in argon gas atmosphere. The surface morphology, composition, crystal structure and optical properties of the resultant Mn2O3 and Ag–Mn2O3 films were studied by field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and UV-Vis spectroscopy. Furthermore, the PEC properties of pristine Mn2O3 and Ag–Mn2O3 composites were compared by linear scanning voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and Mott–Schottky (MS) analyses. On the basis of PEC results, the mechanism of electron transfer is also discussed.

2. Experimental
2.1. Material and methods

All the reagents were purchased from Sigma-Aldrich and purified before use. The synthetic work was carried out under an inert atmosphere of dry argon using a Schlenk tube fitted with a vacuum line and hot plate/magnetic stirrer arrangements. The tetrahydrofuran was rigorously dried over sodium benzoophenolate and distilled immediately before use. The melting point was determined in a capillary tube using an electrothermal melting point apparatus (model MP.D.). Microanalyses were performed using a Leco CHNS 932 elemental analyzer. The Fourier transform infra-red (FT-IR) spectrum was recorded on a single reflectance ATR instrument (4000–400 cm−1, resolution 4 cm−1). The controlled thermal analysis was performed using a Perkin Elmer TGA 4000 thermogravimetric analyzer with a computer interface. The thermal measurements were carried out in a ceramic crucible under an atmosphere of flowing nitrogen (25 mL min−1) with a heating rate of 10 °C min−1. The thin films of the composite were analysed by X-ray diffraction (XRD) measurements by using a PANanalytical, X’Pert HighScore diffractometer with primary monochromatic high intensity CuKα (λ = 1.5418 Å) radiation over Bragg angles ranging from 10 to 90° in a step size of 0.026° while the operating voltage and current were maintained at 30 kV and 40 mA respectively. Raman spectroscopic measurements were carried out on a Renishaw InVia Raman microscope and excitation was performed using the 514 nm
line of argon laser with a 0.01 mW output power. A field emission scanning electron microscope (FESEM, FEI Quanta 400) equipped with an energy dispersive X-ray spectrometer EDX (INCA Energy 200, Oxford Inst.) was used to determine the films’ morphology and chemical composition. X-ray photoelectron spectroscopy (XPS) analysis of the films was carried out using a ULVAC-PHI Quantera II with a 3-channel Spherical Capacitor Energy Analyzer under vacuum (1 × 10⁻⁶ Pa) using Monochromatic Al Kα radiation (1486.8 eV) and a natural energy width of 680 meV. The carbonaceous C 1s line (284.6 eV) was used as a reference to calibrate the binding energies.

The photo-electrochemical responses of the fabricated pristine Mn₂O₃ and Ag–Mn₂O₃ composite thin films were studied by using a Princeton Applied Research (PAR-VersaSTAT-3) electrochemical workstation with a conventional three-electrode system. I–V characteristics were performed through the linear sweep voltammetry (LSVP) technique (potential window range: −0.2 to +1.0 V, and scan rate: 50 mV s⁻¹) while the reference, counter and working electrodes were Ag/AgCl (KCl), platinum wire and fabricated film electrodes, respectively. The PEC test for solar activated decomposition of water was carried out once the electrodes were inserted into the quartz window cell containing 0.1 M Na₂SO₄ aqueous solution in the dark and under light (150 W Xe lamp: 100 mW cm⁻²) conditions.

2.2. Synthesis of [Mn(dmae)₂(TFA)₄] (1)

0.40 g (2.31 mmol) of Mn(CH₃COO)₂ and 0.5 ml (6.2 mmol) of trifluoroacetic acid were added to a 50 ml Schlenk tube containing 20 ml of THF under an argon atmosphere. The mixture was stirred for 6 hours to obtain a clear solution. The solvent was then evaporated under vacuum to obtain a powder which was re-dissolved in 5 ml of THF followed by the addition of 0.228 ml (2.28 mmol) N,N-dimethyl-2-aminooethanol into a 50 ml Schlenk tube. The resulting transparent solution was cannula-filtered and placed at −10 °C for one week to obtain the transparent crystals of complex (1) in 75% yield. Crystals suitable for single crystal X-ray analysis were re-grown from the THF solution. M.p.: 83 °C (decomposition). Elemental analysis: % calculated (found) for [Mn(dmae)₂(TFA)₄] C, 21.11 (20.83), H, 1.77 (1.69), N, 2.05 (1.95). IR (cm⁻¹): 1728(s), 1653(s), 1444(m), 1420(s), 1391(w), 1177(s), 1130(s), 1074(s), 1048(m), 986(s), 852(m), 727(s), 600(m), 502(m). TGA: 179–260 °C (72.77% wt loss) and 260–550 °C (7.06% wt loss); (residual mass of 20.40%); (Cal. for Mn₂O₃ 23.10%).

2.3. Single crystal XRD measurement

Single crystal X-ray diffraction patterns were collected on an Agilent SuperNova Dual diffractometer with an Atlas detector (graphite-monochromatized Mo-Kα radiation, λ = 0.71073 Å) at 100(2) K. The data were processed by using CrysAlisPro, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlisPro) and SADABS multi-scan absorption correction. The structure was solved using the SHELXT program, and refined by the full matrix least-squares method on F² with SHELXL-2014/7. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at calculated positions and were treated as riding on their parent atoms. A drawing of the molecule was produced with XSEED.44

2.4. Deposition of thin films by AACVD

The films were deposited on a commercially available FTO glass substrate of resistivity 8 Ω sq⁻¹ using a self-designed aerosol assisted chemical vapor deposition assembly. The FTO substrates purchased from Sigma Aldrich were cut to the dimension of 25.4 × 12.7 × 2.2 mm (L × W × D) and cleaned prior to use by ultrasonically washing with distilled water, acetone, and then with ethyl alcohol. Finally, they were washed with distilled water, stored in ethanol, and dried in air. Substrate slides of the dimensions of 25.4 mm × 12.7 mm were placed inside a reactor tube and then heated up to the deposition temperature for 10 min to stabilize the temperature before carrying out the deposition. The aerosols of the precursor solution were formed by placing the round bottom flask in a water bath above the piezoelectric modulator of an ultrasonic humidifier. The generated aerosol droplets of the precursor were transferred into the hot wall zone of the reactor by argon gas. The exhaust from the reactor vented directly into the extraction system of a fume cupboard. At the end of the deposition, the aerosol line was closed and only carrier gas was allowed to pass over the substrate. The substrate was cooled to 30 °C before it was taken out from the reactor. In a typical deposition experiment, a homogeneous mixture of 0.10 g (0.60 mmol) of Ag(CH₃COO)₂ and 0.8 g (1.20 mmol) of [Mn(dmae)₂(TFA)₄] (1) was dissolved in 25 ml methanol and utilized for the fabrication of Ag–Mn₂O₃ thin films for 45 min. The carrier gas at a flow rate of 120 ml min⁻¹ was controlled by using a LIX linear flow meter. The deposited light brown thin films are transparent, uniform, robust, and stable towards atmospheric conditions and adhere strongly on the FTO substrate as verified by the “scotch tape test”. Pristine Mn₂O₃ thin films were similarly deposited on FTO under similar conditions by using 0.4 g (0.60 mmol) of [Mn(dmae)₂(TFA)₄].

3. Results and discussion

3.1. Synthesis and characterization of Mn-complex (1)

A mononuclear Mn-complex [Mn(dmae)₂(TFA)₄] (1) (TFA = trifluoroacetate, dmae = N,N-dimethylaminoethanolate) was prepared by the replacement of the acetate ligands by the more strongly chelating TFA and dmae moieties in stoichiometric quantities of manganese(II)acetate dihydrate and trifluoroacetic acid in THF solution as shown in the following chemical equation:

\[
\text{Mn(CH₃COO)₂} \cdot 4\text{H₂O} + 4\text{CF₃COOH} \rightarrow 2\text{(CH₃)₂NCH₂CH₂OH} + \text{THF}
\]

\[
\text{[Mn(CF₃COO)₂O(CH₃)₂N(CH₂)₂] + 2 CH₃COOH + 4H₂O}
\]

The above reaction produced complex (1) in 75% yield in the form of transparent white crystals that were stable in air and...
moisture and soluble in common organic solvents such as methanol, ethanol and THF. The stoichiometric composition of the complex was first ascertained by single crystal X-ray diffraction analysis and was supported by elemental analysis, FT-IR and thermogravimetry. The FT-IR spectrum, [ESI Fig. 1†], of complex (1) indicates that the asymmetric and symmetric $\nu$(C=O) vibrations of the trifluoroacetato ligand fall at 1635 and 1444 cm$^{-1}$ respectively. The difference of 191 cm$^{-1}$ between asymmetric and symmetric $\nu$(C=O) vibrations designates the bidentate nature of the carboxylato groups of the trifluoroacetato ligands that are bonded to the Mn centre.20,21

3.2. Single-crystal X-ray crystallography

The molecular structure of complex (1) is presented in Fig. 1 while geometric parameters and structure refinement details are provided in Tables S1 and S2,† respectively. [Mn(dmae)$_2$(TFA)$_4$] is a monomeric coordination complex in which the “Mn(IV)” cation lies at the center of symmetry. Mn(IV) is coordinated to four oxygen donor atoms from four independent TFA anions and two oxygen atoms from two different dmaeH molecules which occupy the equatorial position, thus, completing the approximate coordination sphere around the metal center. The co-ordination behavior of each TFA anion is monodentate and four oxygen atoms are coordinated with both syn and anti-geometry. Similarly, each dmaeH molecule also acts as a monodentate ligand. No distortion from linearity is observed at the Mn(IV) center and there are no notable interactions found in the crystal structure.

3.3. Thermal studies of complex (1)

The thermal degradation of (1) was examined by thermogravimetric (TGA) and differential thermogravimetric (DTG) analyses performed under nitrogen flow rate of 25 cm$^3$ min$^{-1}$ with a heating rate of 10 °C min$^{-1}$ (Fig. 2). The thermogram shows that the decay process in complex (1) occurs in two successive stages and the first major and rapid decomposition occurs in the temperature range of 179 to 260 °C with a weight loss of 72.77%. The second pyrolysis step is relatively slower and happens in a wide temperature range of 260 to 550 °C yielding a weight loss of 7.06%. The residual mass of 20.17% observed at 550 °C indicates the formation of the expected Mn$_2$O$_3$ oxide material from complex (1) as shown in the following equation:

$$2[Mn(CF_3COO)_4O(CH_2)_2N(CH_3)_2] \xrightarrow{550 \degree C} Mn_2O_3 + Volatile$$

It is reported$^{45}$ in the literature that Ag(OOCCCH$_3$) quantitatively decomposes over a temperature range of 180–280 °C to metallic silver according to the following chemical equation:

$$2Ag(CH_3COO) \rightarrow 2Ag + CH_3COOH + CO_2 + H_2 + C$$

The matching solubility and pyrolysis properties of both Ag(OOCCCH$_3$) and complex (1) prompted us to deposit silver nanoparticles onto Mn$_2$O$_3$ thin films and utilize photoplasmonic interactions of silver for the separation and stability of charge carriers and enhanced absorption of visible light. The procedure adopted for deposition of Ag–Mn$_2$O$_3$ composite films by AACVD and its photoelectrochemical properties are discussed in sections 2.3 and 3.9 respectively.

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![Fig. 1 ORTEP diagram of complex (1) at the 50% probability level.](image1)

![Fig. 2 TGA (black line) and DTG (red line) plots of complex (1) under nitrogen flow at a rate of 25 cm$^3$ min$^{-1}$ and a heating rate of 10 °C min$^{-1}$.](image2)
3.4. XRD analysis
A methanol solution of precursor (1) and its mixture with Ag (CH$_3$COO) were employed in AACVD for the formation of pristine Mn$_2$O$_3$ and Ag-Mn$_2$O$_3$ composite films, respectively, on FTO glass substrates at a temperature of 450 °C. The resultant films were examined by XRD analysis to identify the crystalline and chemical nature of the deposit and both diffractograms are overlaid as shown in Fig. 3. In both cases, the common Mn$_2$O$_3$ phase is in good agreement with the standard ICDD card no. [98-000-9091] (ESI Fig. 2a) and belongs to a cubic crystal system. The characteristic peaks of Mn$_2$O$_3$ indicated by $\bullet$ at 2$\theta$ = 23.0°, 33.1°, 38.3°, 45.0° and 55.2° originate from their Miller indices (012), (112), (222), (004) and (044) respectively. In the Ag–Mn$_2$O$_3$ composite XRD pattern (Fig. 3b), the metallic Ag is identified from its peaks at 2$\theta$ = 38.1° (111), 44.2° (002), 64.5° (022), 77.6° (113) and 81.9° (222) denoted by the symbol $\bullet$ and corresponds well to the standard ICDD pattern number [01-071-6549] (ESI Fig. 2b†). The peaks indicated by * are obtained from the crystalline F:SnO$_2$ of the FTO substrate. These XRD patterns do not show any probable crystalline impurities such as MnO, MnO$_2$ and Mn$_3$O$_4$, Ag$_2$O or AgO. Therefore, we can infer that the methanol solution of precursor (1) and its mixture with silver acetate are capable of generating phase pure Mn$_2$O$_3$ and Ag–Mn$_2$O$_3$ composite films, respectively, at 450 °C through the AACVD method.

3.5. Raman spectroscopy
Pristine Mn$_2$O$_3$ and Ag–Mn$_2$O$_3$ composite films were further examined by FT-Raman spectroscopy as shown in Fig. 4. There appear to be four Raman active modes at 195, 309, 644 and 691 cm$^{-1}$ in pristine Mn$_2$O$_3$ as reported in the literature. These vibrational modes are assigned to out of plane, asymmetric and symmetric bridging oxygen species of Mn–O–Mn. On Ag–Mn$_2$O$_3$ composite formation, the scattering mode of pristine Mn$_2$O$_3$ at 195 cm$^{-1}$ disappears and the band at 309 cm$^{-1}$ remains in its place. The other two scattering modes at 644 and 691 cm$^{-1}$ are shifted to lower wave numbers of 601 and 641 cm$^{-1}$. This lowering of frequencies of Mn–O vibrational modes is perhaps caused by the presence of Ag. No characteristic peak for metallic Ag has been observed as pure metals do not exhibit Raman scattering.

3.6. Surface morphology
The surface morphologies and microarchitectures of pristine Mn$_2$O$_3$ and Ag–Mn$_2$O$_3$ composite films developed at 450 °C via AACVD were examined by FESEM analysis and images are presented in Fig. 5. The surface morphology of pristine Mn$_2$O$_3$ consists of cubical shaped particles with sharp edges which are regularly grown on the FTO substrate making the film compact in nature. However, the Ag–Mn$_2$O$_3$ composite film grown at 450 °C exhibits a different kind of surface topography and various multi-shaped particles including triangular, octahedral, and rod-like objects in the size range of 200–400 nm with clear grain boundaries can be observed on the FTO substrate as presented in Fig. 5b.

The surface compositions of both types of films were analyzed by energy dispersive analysis (EDX) analysis. EDX spectra recorded at various arbitrary large areas (ESI Fig. 3†) revealed that the pristine manganese oxide films contain only Mn atoms throughout the film matrix, while the metallic ratio of Ag : Mn in composite films is found to be 1 : 2 which exactly matches with the formula of the target Ag–Mn$_2$O$_3$ material.

The composite nature of Ag–Mn$_2$O$_3$ was established by EDX map analysis (Fig. 6) and results show that Ag, Mn and O atoms are uniformly dispersed throughout the film matrix.

3.7. XPS analysis
The pristine Mn$_2$O$_3$ and Ag–Mn$_2$O$_3$ composite films were employed in X-ray photoelectron spectroscopy (XPS) to investigate the composition, oxidation states and the electronic structure of the involved atoms and the results are presented in Fig. 7. The survey scan spectra (Fig. 7a) reveal that, except for the O 1s (530 eV) and Mn 2p (640 eV) peaks, the Ag 3d peaks...
emerged with strong relative intensities, showing that Mn$_2$O$_3$ was mainly coated with Ag nanoparticles. In the high resolution Mn 2p spectrum (Fig. 7c) two main peaks at binding energies of 641.10 eV and 653.12 eV, 642.15 eV and 653.83 eV that correspond to Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ have been found for pristine Mn$_2$O$_3$ and Ag–Mn$_2$O$_3$ respectively. The energy difference (Δ) between Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ has been found to be 11.68 eV for Ag–Mn$_2$O$_3$, while the found (Fig. 7c) and the reported value is 12.02 eV for Mn$_2$O$_3$. Hence, an energy difference of 0.34 eV has been found for Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ in the Ag–Mn$_2$O$_3$ composite as compared to pristine Mn$_2$O$_3$. The higher resolution XPS spectrum of Ag 3d was fitted to two peaks at 368.43 and 374.43 eV for Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$, respectively (Fig. 7b). The energy difference (Δ) between Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$

Fig. 5  FESEM images of (a) pristine Mn$_2$O$_3$ and (b) Ag–Mn$_2$O$_3$ composite thin films grown at 450 °C on a FTO substrate.

Fig. 6  Elemental map showing the distribution of Ag, Mn and O elements in the Ag–Mn$_2$O$_3$ composite thin film.
peaks is about 6 eV indicating that Ag mainly exists in the Ag\(^0\) state on the Mn_2O_3 surface. It is worth mentioning that Ag nanoparticles did not show the energy loss events in the form of plasmon peaks in the Ag–Mn_2O_3 composite film perhaps due to the absence of inelastic collisions and interactions between the photoelectrons and deep level electrons. Similar observations for Ag 3d XPS spectra of Ag–TiO_2,\(^{52,53}\) Ag–N-doped TiO_2\(^{54}\) and Ag–ZrO_2\(^{55}\) nanocomposites have also been reported.\(^{56}\)

Meanwhile, the high resolution XPS spectrum of O 1s, Fig. 7d, exhibits asymmetric contours at about 530 eV, attributed to Mn–O in Mn_2O_3. The small peaks at 531 and 532 eV are assigned to the adsorbed oxygen and hydroxyl oxygen, respectively.\(^{57,58}\) The identical electronic structure (Mn 2p, O 1s) confirms the formation of analogous Mn_2O_3 phases in both pristine Mn_2O_3 and Ag–Mn_2O_3 composite films. On the basis of XRD, EDX and XPS results, we infer that pristine Mn_2O_3 and the Ag–Mn_2O_3 composite were successfully fabricated by AACVD in this work.

### 3.8. Optical band gap

The optical band gaps of the as-synthesized pristine Mn_2O_3 and Ag–Mn_2O_3 composite thin films of thickness 270 and 325 nm respectively as measured by using a profilometer were recorded in the UV-visible region of 350–800 nm and are shown in Fig. 8(a and b) respectively. It is obvious from the spectra that both films continuously absorb in the visible region from 400–750 nm. The UV-vis data were applied to Tauc’s formula and direct band gaps \(E_g\) of 2.0 and 1.8 eV were measured for pristine Mn_2O_3 and Ag–Mn_2O_3 composite films, and from their respective Tauc’s plots (insets of Fig. 8a and b). The band gap of 2.0 eV is in good agreement with previously reported values for pure Mn_2O_3 prepared by a different method.\(^{59}\) The lowering of the band gap in the case of the Ag–Mn_2O_3 composite film is attributed to the plasmonic effect of metallic Ag on the Mn_2O_3 oxide. The plasmonic effect of Ag on Mn_2O_3 is also evident from Raman scattering where two bands at 644 and 691 cm\(^{-1}\) are shifted to a lower frequency region. A similar plasmonic effect imparted by silver in attaining a low band gap with better absorbance in the visible region of light has been reported in other metal integrated metal oxide composites.\(^{60,61}\)

### 3.9. Photoelectrochemical studies

The PEC properties of pristine Mn_2O_3 and Ag–Mn_2O_3 composite electrodes were evaluated using a three electrode system.
having a Pt wire and the standard Ag/AgCl as counter and reference electrodes, respectively. The Mn\textsubscript{2}O\textsubscript{3} and Ag–Mn\textsubscript{2}O\textsubscript{3} thin films were used as the working electrodes. 0.1 M Na\textsubscript{2}SO\textsubscript{4} aqueous solution was used as an electrolyte. The separation of the photogenerated electron–hole pairs was evaluated by measuring photocurrents and Fig. 9a shows a comparative study of LSVs of both pristine Mn\textsubscript{2}O\textsubscript{3} and Ag–Mn\textsubscript{2}O\textsubscript{3} composite films at a scan rate of 50 mV s\textsuperscript{−1}. The dark current from −0.2 V to 1.0 V (vs. Ag/AgCl) of each sample was very low. Upon illumination, the Ag–Mn\textsubscript{2}O\textsubscript{3} electrode showed a significant enhancement in the photocurrent density (3.0 mA cm\textsuperscript{−2}) compared to pure Mn\textsubscript{2}O\textsubscript{3} (1.8 mA cm\textsuperscript{−2}) at an applied potential of 0.7 V versus Ag/AgCl. This pronounced photocurrent could be ascribed to the decoration of Ag on Mn\textsubscript{2}O\textsubscript{3}, resulting in a higher separation efficiency of the generated electron–hole pairs and enhanced visible light absorption due to the surface plasmon resonance (SPR) effect.62,63

The Mn\textsubscript{2}O\textsubscript{3} and Ag–Mn\textsubscript{2}O\textsubscript{3} photoelectrodes were further tested under on–off cycle illumination conditions to determine whether the measured photocurrents were associated with the absorption of light. Fig. 9b shows the photocurrent generated under visible light irradiation of Mn\textsubscript{2}O\textsubscript{3} and Ag–Mn\textsubscript{2}O\textsubscript{3} electrodes. A steady and stable photoresponse of 1.8 and 3.0 mA cm\textsuperscript{−2} within 5 on–off cycles could be observed over a 5 min period (Fig. 9b) revealing the higher efficiencies and good stabilities of Mn\textsubscript{2}O\textsubscript{3} and Ag–Mn\textsubscript{2}O\textsubscript{3} photoelectrodes. Moreover, the transient photocurrents agree well with LSV results and strengthen the PEC performance in the visible light region, as well as indicating the existence of the SPR effect of Ag nanoparticles on Mn\textsubscript{2}O\textsubscript{3}.

Electrochemical impedance spectroscopy (EIS) was performed to scrutinize the conductivity of an electrode material, charge transport in the electrode–electrolyte interface and mechanistic analysis of interfacial processes. Fig. 10a displays the Nyquist plots of both pristine Mn\textsubscript{2}O\textsubscript{3} and Ag–Mn\textsubscript{2}O\textsubscript{3} composite films in the frequency range of 0.1 Hz–10 kHz in the 0.1 M Na\textsubscript{2}SO\textsubscript{4} electrolyte in the dark and under visible light illumination. As shown in Fig. 10a, the diameter of the pristine Mn\textsubscript{2}O\textsubscript{3} was much larger than that of the Ag–Mn\textsubscript{2}O\textsubscript{3} composite in the dark as well as under visible light irradiation. The diameter of the semicircle in the Nyquist plots at high frequency represents the charge transfer resistance (R\textsubscript{ct}), which is associated with the electronic properties of the electrode. Under illumination, the R\textsubscript{ct} of Ag–Mn\textsubscript{2}O\textsubscript{3} (∼127 Ω) is considerably lower than R\textsubscript{ct} of Mn\textsubscript{2}O\textsubscript{3} (∼195 Ω). The decrease of the charge transfer
resistance of Ag–Mn2O3 is attributed to the larger number of charge carriers in the electrode sample. It is believed that these charge carriers are produced only because of the presence of Ag inside Mn2O3 which facilitates a faster electron transport and a shorter ion-diffusion path inside the Ag–Mn2O3 electrode. Normally, the smaller arc radius on the EIS Nyquist plot indicates an effective separation of photo-generated electron–hole pairs and a fast interfacial charge transfer process.31 This implies that Ag decoration significantly facilitated the electron mobility by reducing the recombination of electron–hole pairs and contributing to the enhanced PEC performance induced by Ag–Mn2O3.

The frequency dependence phase angle plots (Bode plots) of both pristine Mn2O3 and Ag–Mn2O3 composite electrodes were recorded for the detailed understanding of the charge-transfer resistance phenomenon in these materials. The Bode phase plots obtained for the Mn2O3 and Ag–Mn2O3 thin films are shown in Fig. 10b where the characteristic frequency peaks were affected in the dark and under light conditions.

In a dark environment, the Mn2O3 and Ag–Mn2O3 films showed the frequency peak maxima ($f_{\text{max}}$) at 13.7 and 9.79 Hz respectively, suggesting larger charge-transfer resistance at the electrode/electrolyte interface due to a lack of availability of the electroactive species. However, the $f_{\text{max}}$ is observed to shift toward the low frequency region (~1 Hz) in the presence of light indicating a rapid electron-transfer (conductive) behavior of the Mn2O3 and Ag–Mn2O3 films. It is worth noticing that the phase angle values of Mn2O3 and Ag–Mn2O3 are increased in the dark, revealing the conducting nature of the films. The phase angle of 90° or above signifies the ideal capacitive nature of the electrode.64 In the present case, still the phase angle of pristine Mn2O3 and Ag–Mn2O3 in the dark and under illumination is much less than 90° which suggests that the electrode does not behave like an ideal capacitor. These characteristic frequencies can be used to calculate the electron recombination lifetime ($\tau_n$) of the corresponding material using the following relationship:54

$$\tau_n = 1/2f_{\text{max}}$$

where $f_{\text{max}}$ is the frequency peak maximum. The recombination lifetime ($\tau_n$) values for the pristine Mn2O3 and Ag–Mn2O3 composite films are calculated to be 11.6 and 16.2 ms, respectively in the absence of light. It is well known that when Ag nanoparticles are deposited on the metal oxide surface, the plasmon resonance energy transfer (PRET) from Ag to metal oxide would occur.35 This PRET process would establish an oscillating electric field which would reduce the recombination of photo-generated electron–hole pairs. Therefore, the lifetime of charge carriers in Ag–Mn2O3 is prolonged effectively compared to pristine Mn2O3.

Further Mott–Schottky (MS) experiments for pristine Mn2O3 and Ag–Mn2O3 composites were conducted to deduce information about the type of semiconductor, the flat band potential and the charge density values. Fig. 11 shows that both Mn2O3 and Ag–Mn2O3 show a positive slope in the MS plots, as expected for the n-type semiconductor.

Importantly, the considerably smaller slope of the Ag–Mn2O3 composite in the MS plot represents a higher carrier concentration compared to pure Mn2O3. The flat band potential of the Ag–Mn2O3 composite, −0.91 V/SCE, is observed to be lower than −0.22 V/SCE of pristine Mn2O3, indicating better transportation of the photogenerated carriers in the case of the Ag–Mn2O3 composite. Also the carrier densities of both pristine and composite films were calculated to be $1.62 \times 10^{13}$ and $3.09 \times 10^{13}$ cm$^{-3}$ respectively. In the Ag–Mn2O3 composite thin film, Ag is the source of extra charge carriers. A higher charge carrier concentration in the composite film has an influence on changing the work function of the material which enhances the charge transfer at the electrode–electrolyte interface and an improved PEC performance.

The markedly enhanced photocurrent of the Ag–Mn2O3 film electrode is a direct consequence of the synergistic effects of the uniformly dispersed Ag on the Mn2O3 structure. On the basis of PEC results, we have proposed a mechanism of electron transportation from Ag to Mn2O3 as shown in Scheme 1. Upon visible light illumination of the thin film electrons are excited from the valence band to the conduction band of Mn2O3 and then migrate to Ag nanoparticles where they are
photo-excited and generate hot electrons on its surface due to
the surface plasmon resonance. The plasmon-induced hot
electrons are introduced back into the conduction band of
Mn$_2$O$_3$, and then to the FTO substrate through the Mn$_2$O$_3$
backbone. The generated holes on the surface of the thin films
react with water to produce oxygen and hydrogen ions. Finally,
the electrons are transferred to the Pt electrode where hydro-
gen ions are reduced to hydrogen.

4. Conclusion

In summary, pristine Mn$_2$O$_3$ and Ag–Mn$_2$O$_3$ composite film
electrodes have been developed on FTO glass substrates utiliz-
ing a newly synthesized complex (1) and its mixture with Ag
(CH$_3$COO) via an aerosol assisted chemical vapor deposition
(AACVD) technique. The decoration of Ag nanoparticles on
Mn$_2$O$_3$ not only reduces the band gap by the SPR eff
ect but
also enhances the light-harvesting effi
ciency and suppresses
the recombination of the photogenerated electron–hole pairs,
thus enhancing the overall water-splitting reaction. The as-
synthesized Ag–Mn$_2$O$_3$ composite photoelectrodes yielded a
high photocurrent of 3.0 mA cm$^{-2}$ at a potential of +0.7 V
versus Ag/AgCl, which is 1.6 times higher than that of the
pristine Mn$_2$O$_3$ film. The Ag–Mn$_2$O$_3$ nano-composite system
studied here could be extended to other metal–metal oxide
semiconductors for their solar conversion applications.

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References

1 G. Li, L. Wu, F. Li, P. Xu, D. Zhang and H. Li, Nanoscale,
2013, 5, 2118–2125.
3 M. M. Momeni, Y. Ghayeb and M. Davarzadeh,
805–811.
5 J. Yan, Q. Ye, X. Wang, B. Yu and F. Zhou, Nanoscale, 2012,
4, 2109–2116.
6 R. H. Gonçalves, L. D. Leite and E. R. Leite, ChemSusChem,
2012, 5, 2341–2347.
7 J. Su, X. Feng, J. D. Sloppy, L. Guo and C. A. Grimes, Nano


