In-site Preparation and Characterization Catalytic-Composite Used for Plastic Waste Degradation to Fuel.

Ameen Abdelrahman (chem.shah@hotmail.com)
Beni Suef University

Asmaa S. Hamouda
Beni-Suef University: Beni Suef University

A.H. Zaki
Beni Suef University

Research Article

Keywords: polyethylene high density (PEHD), gas yield, graphene, (Ag, Mn) NPs, polyethylene glycol (PEG), gasification, pyrolysis

DOI: https://doi.org/10.21203/rs.3.rs-555101/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License
Abstract

In order to get renewable energy from plastic waste, it should find a pathway or create a new composite that is thermally stable, non-toxic, environmentally inexpensive, and highly efficient. Thus, in our research, we work with composite materials that provide a hetero catalyst designed to crack Polyethylene high Density (PEHD), which is composed of Metals (Mn, Ag) in Nano scales, and Graphene impregnated inside the PEG matrix. In order to evaluate fabricated composite catalyst, to be applicable on conversion plastic polyethylene high density to gases yields and solid char carbon using pyrolysis and gasification reaction. The process were carried out inside the fixed bed reactor. Various characteristics have been conducted for final products (gases and black char), further spectroscopic analyses like Ultraviolet–visible spectroscopy (UV), Cyclic voltammetry (CV), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), and Thermogravimetric analysis (TGA) were investigated for the new composite.

1. Introduction

Recently, scientists and materials engineers gave more attention to manganese oxides due to their unique catalytically activity as transition metals as well as their distinctive physical and chemical properties, and wide applications in organic conversion catalysis, ion exchange, molecular adsorption, biosensor, and energy storage [1–9]. Its electrolytes are a solution for renewable batteries [10]. Various methods have been reported to synthesize MnO$_2$, including thermal decomposition [11], template method [12], and hydrothermal reaction [13]. Various studies and research on the efficiency of catalytic composites in reforming cracking and selective oxidation of organic compounds [14–17] were presented, including noble metals (Au [18, 19], Pd [20], Pt [21], Ru, Cu, Ir [22], etc.) As an addition to bimetallic compositions application [20]. Silver has unique characteristic such as stability (resists oxidizing); ability to transform into a cluster due to high dispersion on a different substrate to form one homogenous phase; and synergistic activity on many other modifiers such as transition metal, and noble metals. For that reason, silver receives special attention from scientists and materials scientists in different fields [23–27].

Since 2004, Graphene has gathered more attention and interest in different application fields, especially material science, for its unique two-dimensional (2D) structure, mechanical properties and physical properties [28–30]. Furthermore, because of its existence and economic value, it was used instead of various materials such as metals, ceramics and carbonaceous fiber materials. New materials like helping polymers, graphene, and carbon nanotube increase the efficiency of ITO transparent conductors [31–33]. Graphene-based TCFs are a promising material to deal with these problems [34, 35]. Scientists and materials engineers used different techniques to synthesize graphene by physical and chemical methods such as Chemical Vapor Deposition (CVD), Epitaxial growth, Mechanical Exfoliation, and reduction of graphite oxide [36, 37]. In addition, transparent graphene has been created using various processes like directly conveying it through the CVD Technique, vacuum filtration and Langmuir–Blodgett (LB) assembly [38–40].
Although Graphene is not well dissolved in an organic solvent, it has the ability to join and fill out voids between interaction layers in other components in one phase such as clays and polymeric matrix. That is due to superior mechanical and thermal properties of graphene nano powders. Then it improves and enhancements the crosslink of the overall structure [41]. Graphene is considered as an environmentally friendly product. It is also inexpensive; thus, it replaces much of the catalyst. Another advantage of graphene-like exfoliated and cost-effective method has been described by Fukushima et al. [42–45]. On the other hand, graphene is characterized by electrical and thermal properties. It enforces and enhances other materials. Kulkarni et al. [46] worked on colloids (Nano fluids) that utilize metals oxides such as CuO, Al$_2$O$_3$ and SiO$_2$ nanoparticles spread out in a 60/40% EG-water mixture to count the convective heat transfer coefficient and the viscosity of Nano fluids. Sundar et al. [47] also studied another 50/50% EG-water contain nanoparticles metal oxides, Al$_2$O$_3$ and CuO, to investigate the thermos-physical properties of the prepared mixture.

For this study, we created composite materials that operate as a heterogeneous catalyst for conversion plastic waste (PEHD) to create energy throughout the thermal and catalytic processes of degradation. Composite made from the strain of metallic nanoparticles (Silver, and Manganese) was assembled on a thin layer of Graphene inside polyethylene Glycol polymeric matrix. Our analysis and characteristics related our new composites and their application are discussed below.

2. Material And Methods

2.1. Materials. All chemicals used were of AR Sigma Aldrich grade, from Egypt. Manganese Sulfate, Manganese Oxalate, organic solvent (acetone, alcohol), silver nitrite, Nano powder graphene were delivered from Loba Cheme (India). High Density Polyethylene (HDPE B1054) was purchased from, SABIC, Egypt.

2.2 Methods

2.2.1 Preparation of Catalyst

2.2.1.1 Preparation of MnO$_2$. Use the Co-precipitation method, which dissolves two anions Manganese salts (II), Sulphate and Manganese Oxalate. Take the same 0.2 M from the concentration of both, blend continuously, then stir them ultrasonically at 60°C for 45 min. Add a few drops of NaOH solution to keep pH of the solutions at 12. Cool down at ambient temperature, filter, and wash with ethanol. Lastly, dry the precipitates, and then put in a muffle furnace at 500°C for 5 h [48].

To obtain the precursor Ag -NPS we used Silver Oxalate to graft and assemble the Silver over the Graphene thin layer. Then, we immersed the result inside a PEG matrix. We dissolved 1.5 g of Silver Nitrate (purity ≥ 99.0%, Sigma Aldrich) in 20mL deionized water, and then added the liquid to the Oxalic Acid solution at 60°C. This solution is prepared (2:1 M ratio) with 1.48g Oxalic acid dehydrated in 40mL distilled water at 60°C [49–51]. Once you obtain the Silver oxalate precipitate, filtrate with washing with Water and Ethanol. The powder will dry overnight at 60°C under static air.
2.2.1.2 Colloidal solution preparation. This solution is made by dissolving 1.18 g of white powder (Silver Oxalate) immersed inside 40 ml of a mixture composed of Mn and dispersed in a Graphene Nano powder (Sigma Aldrich) solution prepared for a couple of days (Graphene particles exaggerated). Then ultrasonic stirring must continue at 60°C for 6 h. The composite of Graphene-Ag configured, dried overnight, will result in a composite of graphene /Ag and Mn NPS.

2.2.1.3 PEG-Ag-graphene matrix. The composite was synthesized using microwave irradiation. Take 5 g PEG5000 (Sigma Aldrich, Egypt) in dry round bottom flask, and set up Polyethylene Glycol solution with a condenser associated with Milestone MicroSynth microwave (Italy). PEG solution must be irradiated for 8 min at 1100 W and 120°C to be melted and viscous. To form a composite, add 1 g of prepared Graphene-Ag composite and 5 gm dried viscous PEG, put together inside a microwave; then, irradiate and stir everything at 1100 W and 25 rpm at a constant temperature of 130°C for 20 min. Then, the composite will be ready to characterize and applicable [52] as shown in Fig. 1.

2.2.2 XRD analysis. The MnO2 filter is transferred to RETSCH Planetary Ball Mills Type PM 400, then crushed using the ball mill at speed 150 rpm for 5 h to get Nano size structure, then prepared samples were carried out using X-ray diffraction patterns. It's a Pan Analytical Model X’ Pert Pro, which was outfit with CuKα works at radiation (λ = 0.1542 nm), Ni-filter associated with the detector. The diffractograms were investigated at a 2θ range of 0.5°–90° and size of 0.02 Å. All measurements were conducted at the Research Central Metallurgical Research and Development Institute.

2.2.3 TEM characterize. All samples characterized were carried out using Transmission electron Microscopy (TEM) Model: JEOL JEM-1230 operating at 120 kV associated specifically a CCD camera. All analysis has been done at the National Research Centre. Measurements of samples conducts were done using a convenient method of prepared samples to get good results throughout the TEM image utilizing copper grids on an amorphous carbon film.

2.2.4 Particle size analyzer. Particle analysis has been investigated at Cairo university using Zetasizer Nano S90 (Malvern) modal Nano S90. It is run by Red laser as Zetasizer instrument at a 90° angle.

2.2.5 Prepared samples of suspended Nano particles had been characterized using Ultraviolet-visible (model UV-1800 Shimadzu UV spectrophotometer). The spectral analysis for silver and Manganese samples is investigated around a wavelength of 150 e was 1000 nm. All measurements have been done at Beni Suef University.

2.2.6 Pyrolysis and gasification processes were carried out using a fixed bed reactor, which is heated using an electrical furnace. The pyrolytic system is set up in environment department, Beni Suef University.

2.2.7 Gaseous yield products were characterized using Gas chromatograph ( GC), a VARIAN model CP-3800. All gas samples measurements were carried out at the Egyptian Petroleum Research Institute (EPRI), Nasr city, Cairo.
3. Results And Discussion

3.1 Characterization and study of the physical properties of the composite.

Crystalline graphic structure of both Prepared MnO₂, and Ag NPs have been investigated by X-ray diffraction, as reported in Fig. 2. This figure illustrates ranges of diffracted intensities registered at 20 matches to planes of (1 1 1), (2 0 0), (2 2 0) and (3 1 1) respectively. These clear out the cubic crystal structure of silver, whose corresponding (d calculated) values are 2.336, 1.955, 1.436 and 1.224 Å for (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes respectively, as seen below in the same figure [53]. Moreover, they coincide with standard silver values using the Debye-Scherrer formula:

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

The silver nanoparticles crystallite calculated is ~25 nm, confirmed by using the TEM characterize in Fig. 3. On the other hand, the recorded peak positions (2θ, degree) of Mn-NPS are 18.18, 37.48, 42.82, 58.81, 6.21, 74.58 and 78.43 respectively. The average crystalline size calculated using the Debye-Scherrer formula is about 25–30 nm.

The TEM image (Fig. 3a, b) shows the average size of both Manganese and Silver particles is 25–30 nm. The Graphene surface sheet contains spread large numbers Mn nanoparticles demonstrated in Fig 3a, which it is based on electronic configuration half fill d-orbitals. These facilitate electron transfer related to oxidation-reduction on the surface of graphene. Another observation is the presence of some floccules and aggregates that appear in Fig. 3a. These could be the immobilization and deposition of Manganese oxide on Graphene surface, or metallic conjugated bonds between Mn+/Mn²⁺ and Ag+/Ag⁻, as shown in Fig. 3d.

Suspended graphene particles disperse in polyethylene Glycol as demonstrated in Fig. 3c. The average size of a particle is 110 to 440 nm. Variety of particle size is due to the aggregation and flocculation of the same units of same graphene. Furthermore, the viscosity of polyethylene glycol effected on particles volume. With regard to Fig. 3d describes surface morphology of novel composite; there is a complete distribution of numerous of nanoparticles (Mn, Ag, and Graphene) inside PEG matrix of different sizes around 10–30 nm⁻¹, in addition to the flocculation and deposition of particles on the surface of PEG. Particles deposition is the return of interaction forces, spaceman spherical, and viscous nature of solution.

Composite Thermal analysis. Figure 4a illustrates HDPE decomposition at a flow rate of 10°C/min. A PEHD sample was carried out using a thermal gravimetric analyzer (TGA). Fig. 4b points out the change in the mass fraction of the sample with a function of temperature at different heating rates. Heating rates range from 400 to 520°C, which shows how similar behavior can be within a single mass loss zone. Degradation zone is approximately centered at 425, 450, and 460°C at a heating rate of 10°C/min. The
temperature reforming zone of HDPE ranges between 380–510°C. Major mass loss in that stage relates to the elements of CO₂, water, H₂, and light components molecules breakdown of the polymeric chain.

On the other hand, thought PEG thermal degradation starts low, from 100 to 390°C, losing some molecules like CO₂ or water causes only a slight change in its appearance. But in the case of PEG-graphene, the TGA has become higher and requires more heat to dissociate and reach 410°C. This is lower comparing with PEG-NPS in Fig. 4b, whose degradation point is 425°C. In consequence, we prepared composites with degradation at 460°C. Also, it is confirmed that nano metals (Ag and Mn) filled out interspace and irregularly distributed voids of PEG. This leads to a decreased molecular weight and an increased melting point of composites. Furthermore, TGA of the prepared composite is closer to the temperature of fixed bed reactor, which was confirmed by another characterizations such as EDX and TEM.

Figure 5 illustrates the suspended particles in liquid phases. That technique shows the qualities and quantitative analysis used to investigate particle size and shape. The same figure explains different size particles for different prepared solutions. We have three solutions containing (magnesium, and sliver) nanoporticals solution, graphene suspended in (Ag, Mn) nanoparticles solution, and mixture of composites (Ag, Mn, Graphene, and PEG). We recorded a strong peak in anoparticals solution that appears at 110 nm, which is lower then in PEG solution, and composite 220, and 590, 890 d.nm respectively. Our interpretation is that the force interaction (shear strength results from PEG apparent viscosity, coated the entirely nano metals particles and different conjugated bonds between nanoparticals together cause a massive particals. PEG viscosity has an effecting factor on particle movement and increasing enhancement crosslinked inside a matrix, due to stability of composite during thermal degradation.

We used the UV to illustrate the different signals and spectra of prepared samples. We have three samples: solution of PEG/Metals NPS, PEG/Graphene, and matrix of their solution prepared as shown in Fig. 6. Comparing different curves we found specific spectra characting Ag, whose absorbance slightly shifted at 430 nm due to cross-links with polyethylene glycol through a hydrogen bond. Besides, the graphene in the second curve, which is also shifted, could be the resonance of bi bonds in addition to the contact with polyethylene glycol. The UV-Vis spectrum for this (PEG/graphene /Metals NPs) composite disappeared with existence of wide board peak, it could be surface plasmon resonance of spherical nanoparticles nature, or metallic bonds created between Mn-Ag. That shift is represented in Fig. 6 at 410 and 450 nm. That is good evidence that indicates all nanoparticles (Mn, Ag, and graphene) assembled and impregnated inside PEG matrix [54].

3.2 Electrochemical analysis

Cyclic voltammetry (CV) is one of the most important techniques used to measure the rate of oxidation and reduction reaction species in the prepared solution. To conduct that experiment, we need to set up three cell electrodes, and reference, working, and counter electrodes to measure variation change between current and volts. We found a difference of current based on the change of reaction metals (Sliver
and Manganese metals. Figure 5 shows different potential states released from electrochemical series of metals nanoparticles. A slight peak appears at cycle voltammetry curve (-V) 1.2, and (+V) 1.2; it is due to reversible reaction occurred: according the previous equation $\text{Mn}^{+2}$, oxidase to be $\text{Mn}^0$ to give a pair of electrons, on the other side and Ag is gain electron to be a reducing agent (reversible reaction). That appears in Fig. 7 at electrochemical potential equal (+1.6) V. In conclusion, there are Nemours ions charge transfer through a solution, but on the other hand, the transfer is demolished due to high viscosity of polymer, which restricts that ions transfer, although it is a protonic solution, and many interface interactions dependable on and van der Waals force mechanism.

Throughout the Cyclic voltammetry (CV) analysis, we concluded that there are various electrochemical reactions occurring between different species of chemical reactions. For instance, Mn has a different (+2, +3, ..., and + 5) valence oxidation state to reach stable (half or empty) state in electronic configuration of (d-orbital); therefore, it has a tendency to lose pairs of electrons, which reduces silver metals and creates serious electrochemical reaction mechanisms. Graphene works as bridge to transfer the charge between both metals sides. Due to $\pi$-$\pi$ bonds of graphene structure, which lead to electron resonance and reaction stability, our investigation follows Eq. (1):

$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} + E^\circ_{\text{oxidation}}$$

**Half-reaction mechanism for each process.**

\[
\begin{align*}
\text{Mn(s)} & \rightarrow \text{Mn}^{2+}(\text{aq}) + 2 \text{e}^- & E^\circ &= +0.8 \\
\text{Ag}^+(\text{aq}) + \text{e}^- & \rightarrow \text{Ag(s)} & E^\circ &= -2.21
\end{align*}
\]

**Graphene**

\[
\text{Ag(s)} + \text{Mn}^{2+}(\text{aq}) \quad \leftrightarrow \quad \text{Ag}^+(\text{aq}) + \text{Mn(s)}
\]

Graphene is work as a bridge (electrolyte membrane).

The storage charge is based either on the adsorption of cations at the surface of the electrode material or on the intercalation of cations in its bulk.

One of the important values to using Ag as a support catalyst are its nature and activity as a reducing agent. It has a great effect on free energy according equation $\Delta G = \Delta H - T\Delta S$, then that reaction will shifted to products and became the exothermal reaction. Moreover, it employs as an accelerator for the reaction (between graphene surface assembled Mn NPS as the active species and plastic PE). It is due to down heating rate of reaction during the decomposition process.

On the other hand, the average size of Mn and Ag NPs is down 30 nm. Tiny size of Nano metals causes the disorder dispersal on Graphene surface to make chelating complex then immersed inside PEG matrix.
Thus there were created many active sites, which accelerated the reaction (reducing both of reaction time and heating rate of cracking process). Complete cracking was performed at 600°C instead of 750°C without the catalyst additive.

3.3 Evaluating the prepared Composite’s impact on Plastic Waste conversion to Energy.

3.3.1 Pyrolysis system. Pyrolysis and gasification were investigated using a fixed bed reactor (SS 310, 0.92 mm ID). This reactor height is 36 cm. The reactor is heated using an electrical furnace. The reactor has a joint inlet and the outlet continues throughout the union connection. The upper portion includes two valves that monitor pressure gauge to measure pressure during the test as shown in Fig. 8. PEHD plastic sample and additives are placed together in the bottom section of the reactor. This was in the case of self-purging pyrolysis (100% N\textsubscript{2}) for 5 min. However, in the case of gasification we used air (Oxygen). We took 2 g of pure HDPE with or without composite and using different loaded ratio of prepared catalyst during 45 min at 700°C, then placed the packed stuffed reactor inside the furnace adjustable at the reaction temperature. The electrical furnace (65x8x25 cm\textsuperscript{3}), associated with a thermocouple, has a temperature controller during the reaction. After a given reaction time, when reaction is done, the reactor is taken out of the furnace, then cooled at room temperature. Later, the yield gases are collected using sampling bulbs – glass to quantify and analyze. Also, char (black carbon) was collected and weighted.

3.3.2 Studying the optimized parameters of degradation. Figure 9 points out the degradation set-up of sample Polyethylene at high Density. It should select specific parameters to obtain high efficiency of gases and solid waste. There are various factors affecting reaction mechanisms such as Temperature, the catalyst used, Time of reaction, and Pressure. We reported a gradual increase for pressure and temperature for one hour to be stable at 750°C. We reached the ideal parameters for conducting experiments. After thermal degradation at 700°C for one hour, all products are gases and solid waste without liquid and tar, which cause serious problems. They can plug or block the Reactor tube.

To evaluate our composite, we applied that composite polymeric materials (graphene/nano Metals/PEG on the catalytically cracking of plastic waste (PEHD) to fuel using two different techniques (pyrolysis and gasification) at the same selective optimized reaction parameters. We used one gram of PEHD (raw materials) plus 0.06% of the catalyst in case of a catalytic cracking reaction and no-additives in thermal cracking.

Figure 10 shows the distribution of gas release and solid waste (Char) resulting from the use of 1 g of PEHD (plastic) in a continuous catalytic process in a Fixed bed reactor at a constant temperature of 700°C (the best temperature recorded in the previous experiment).

The Gasification process lasts an hour, at 700°C. We noticed the diversity of products (gas, and char) in gasification without a catalyst. In case of catalyst existence we reported an increasing of the yield of reforming gases and a decreasing of solids waste (char). That is a good indicator of complete conversion of plastic. Fig. 11 illustrates that gases yield increases as soon as temperature goes from 0.7 to 0.83 m\textsuperscript{3}/kg. The char yield reaches 6 wt % at 600°C and 13.6 wt % at 700°C.
These results are completely different in gasification pyrolysis when the prepared catalyst is not added. For instance, char still exists in large amount until the end of the reaction at 700°C. Further, the rate of gas yield is not the same resulting from catalytic gasification, which ranges between 0.42 and 0.46 m³/kg. That will confirm our new catalyst successfully decreased reaction activation energy, and then accelerated the reaction rate.

Figure 12 explains thermal and catalytic pyrolysis. We recorded two important observations: a) effecting of 0.06 wt % of composite catalyst on the scenario of reaction (Reduced rate; and Time of reaction); b) distribution of gases and black carbon char in the presence of a catalyst. In existence of 0.06 wt % of prepared composite, we found an increase in gases yield-up to 0.47 compared to 0.38 in thermal pyrolysis degradation. On the other hand, in case of catalyst, we found the quantity and qualities of solid char carbon are more than in thermal pyrolysis (without catalyst as shown in the figure: catalyst char wt % gradually increases from 0.25 to 61.6 compared to incase presence of 0.06% wt % of the prepared composite catalyst, char wt % slightly increases from 0.25 to 45.5, then it declined to 22.3. That is good evidence for optimal conditions, such as a loading catalyst value, temperature 700°C for 45 min reaction time, sufficient to complete degradation of PEHD.

3.3.3 Characterization of gas yield distribution from gasification.

Petro-chemical reaction is considered as one of organic mechanisms, such as deformation, cracking and oxidation of light hydrocarbon olefins from gaseous and alkanes addition to aromatic and organic compounds. Our reaction is based on two types of mechanism. In pyrolysis (absence of oxygen), various paraffin compounds (C₃–C₄) dehydrate and thermally crack to the mixture of Olefins (Ethylene, Propylene, and Methane). In Gasification (Oxidation), we have two another possibilities – someorganic and aromatic compounds (Benzene, Toluene, and Benzoic cyclic) are formed. Additionally, many hetero-cyclic compounds form due to the number of optimized reaction conditions such as the catalyst activity, nature of cracking materials, and temperature during the process.

Both mobility of lattice oxygen (it is responsible for forming hydrogen bond) and the tiny size of Mn facile the oxidizing reaction in existence on all reactants surface. Furthermore it could be a high effective on gasification process. Thus, with the loss of electron, the oxidation is gained by Ag metals and the remaining electron is easier to move throughout the d-Orbital electronic configuration and might resonate bi-bonds inside graphene. In conclusion, resonance impact reduces the heating temperature reaction of both gasification and pyrolysis process. Furthermore, the stability of the new composite by new metallic bonds (Ag–Ag and Mn–Mn) increased. The enhancement of composite thermal and physical behaviors-based on reducing inter-layer crosslink voids space.

During the gasification process, there is hydrocarbon oxidation, which results from the decomposition of polyethylene high-density, and leads the elimination of water molecules. We recorded a higher quantity of hydrogen (renewable energy) in gasification than pyrolysis. This could be produced by bonding two hydrogen atoms. Moreover, MnO plays a vital role in deforming polymeric materials to convert hydrogen
and methane. Also, the amount of methane gasification (91.3 wt %) is bigger than in pyrolysis (77.2 wt %). Meanwhile, the graphene mechanism also has a great effect on the distribution of the products (Fig. 13). It appeared that the number of aromatic compounds formed during degradation. It could be back covalent bond as well as free ions π-π, which help elongated saturated chain or more than C₆−C₇ such as toluene and hexane.

3.3.4 PEHD char solid product analysis. Figure 14 illustrates the surface morphology of a prepared composite released from the decomposition. The surface is rough with some metallic brightness due to silver nanoparticles, added to flocculated layers, and massive residual PEG particles. That is also, clear stability of composite reached under high temperature (750°C).

We used EDX analysis to detect element analysis of the char composition. It appeared numerous of the elements, which are the main components of our composite, such as silver, Manganese and carbon structure and some impurities such as additives. Also it confirmed thermal stability of our composite under optimistic degradation process. Moreover, Fig. 15 agrees with previous data pointed in different figures.

4. Conclusions

In our research, we created new composite-working as a catalyst, using degradable plastic waste to create sustainability energy, one of our daily life requirements. It is an economic, non-toxic, biodegradable, highly sustainable, and affordable solution, which is also highly efficient during the reaction process. That composite is made of Nano metal particles assembled on Graphene, impregnated inside a PEG polymeric solution. Various methods and techniques have been used to study and evaluate our composite in a different range of processes and applications. The unique properties and wide range of these catalysts applications in all aspects of life (biomedical, industrial, environmental, and communication) make them interesting in Materials Science and Engineering.

Abbreviations

MnO₂: Manganese Oxide
PEHD: Polyethylene high density
PEG : Polyethylene glycol
TO : Transparent conductors
LB : Langmuir–Blodgett
EG : Ethylene Glycol
CVD : Chemical vapor deposition
Declarations

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

Data Availability

Data and materials are available under requests.

ADDITIONAL INFORMATION

Ameen Abdelrahman  https://orcid.org/0000-0002-7177-2687
Ayman Zaki  https://orcid.org/0000-0003-0026-1721
Asmaa S. Hamouda  https://orcid.org/0000-0002-1991-2347

References

1. Li, W. N., Yuan, J., Shen, X. F., Gomez-Mower, S., Xu, L. P., Sithambaram, S., ... & Suib, S. L. Hydrothermal synthesis of structure-and shape-controlled manganese oxide octahedral molecular sieve nanomaterials. Advanced Functional Materials, 16(9), 1247-1253 (2006).

2. Yan, J., Khoo, E., Sumboja, A., & Lee, P. S. Facile coating of manganese oxide on tin oxide nanowires with high-performance capacitive behavior. ACS nano, 4(7), 4247-4255(2010).

3. El-Deab, M. S., & Ohsaka, T. Manganese oxide nanoparticles electrodeposited on platinum are superior to platinum for oxygen reduction. Angewandte Chemie International Edition, 45(36), 5963-5966(2006).

4. Liu, D., Zhang, Q., Xiao, P., Garcia, B. B., Guo, Q., Champion, R., & Cao, G. Hydrous manganese dioxide nanowall arrays growth and their Li+ ions intercalation electrochemical properties. Chemistry of Materials, 20(4), 1376-1380(2008).

5. Wang, L., Sakai, N., Ebina, Y., Takada, K., & Sasaki, T. Inorganic multilayer films of manganese oxide nanosheets and aluminum polyoxocations: fabrication, structure, and electrochemical behavior. Chemistry of materials, 17(6), 1352-1357(2005).
6. Fei, J. B., Cui, Y., Yan, X. H., Qi, W., Yang, Y., Wang, K. W., ... & Li, J. B.. Controlled preparation of MnO2 hierarchical hollow nanostructures and their application in water treatment. *Advanced Materials, 20*(3), 452-456(2008).

7. Wang, X., & Li, Y. Selected-control hydrothermal synthesis of α-and β-MnO2 single crystal nanowires. *Journal of the American Chemical Society, 124*(12), 2880-2881(2002).

8. Li, Z., Ding, Y., Xiong, Y., Yang, Q., & Xie, Y. One-step solution-based catalytic route to fabricate novel α-MnO2 hierarchical structures on a large scale. *Chemical communications, (7),* 918-920(2005).

9. Zhang, H.. Molecularly imprinted nanoparticles for biomedical applications. *Advanced Materials, 32*(3), 1806328(2020).

10. Simon, P., & Gogotsi, Y.. Materials for electrochemical capacitors. *Nanoscience and technology: a collection of reviews from Nature journals*, 320-329(2010).

11. Yu, C. Y., Chu, C., Chou, S. J., Chao, M. R., Yeh, C. M., Lo, D. Y., ... & Huang, K. C. Comparison of the association of age with the infection of Salmonella and Salmonella enterica serovar Typhimurium in Pekin ducks and Roman geese. *Poultry science, 87*(8), 1544-1549(2008).

12. Fei, J., Cui, Y., Yan, X., Yang, Y., Wang, K., & Li, J. Controlled fabrication of polyaniline spherical and cubic shells with hierarchical nanostructures. *ACS nano, 3*(11), 3714-3718(2009).

13. Subramanian, V., Zhu, H.W., Vajtai, R., Ajayan, P.M., and Wei, B.Q., Hydrothermal Synthesis and Pseudocapacitance Properties of MnO2 Nanostructures, J. Phys. Chem. B, , vol. 109, pp. 20207–20214 (2005).

14. Kopylovich, M. N., Ribeiro, A. P., Alegria, E. C., Martins, N. M., Martins, L. M., & Pombeiro, A. J. Catalytic oxidation of alcohols: Recent advances. *Advances in organometallic chemistry, 63*, 91-174 (2015).

15. Mobley, J. K., & Crocker, M. (2015). Catalytic oxidation of alcohols to carbonyl compounds over hydrotalcite and hydrotalcite-supported catalysts. *Rsc Advances, 5*(81), 65780-65797.

16. Ciriminna, R., Pandarus, V., Béland, F., Xu, Y. J., & Pagliaro, M. Heterogeneously catalyzed alcohol oxidation for the fine chemical industry. *Organic Process Research & Development, 19*(11), 1554-1558(2015).

17. Xu, C., Zhang, C., Li, H., Zhao, X., Song, L., & Li, X.. An overview of selective oxidation of alcohols: Catalysts, oxidants and reaction mechanisms. *Catalysis Surveys from Asia, 20*(1), 13-22 (2016).

18. Sharma, A. S., Kaur, H., & Shah, D.. Selective oxidation of alcohols by supported gold nanoparticles: recent advances. *RSC advances, 6*(34), 28688-28727(2016).

19. Hussain, M.A., Joseph, N., Kang, O., Cho, Y.-H., Um, B.-H., and Kim, J.W., Supported Metal Nanoparticles: Their Catalytic Applications to Selective Alcohol Oxidation, *Appl. Chem. Eng.,* , vol. 27, pp. 227–238(2016).

20. Sharma, A. S., Kaur, H., & Shah, D. Selective oxidation of alcohols by supported gold nanoparticles: recent advances. *RSC advances, 6*(34), 28688-28727(2016).

21. Liu, F., Wang, H., Sapi, A., Tatsumi, H., Zherebetskyy, D., Han, H. L., ... & Somorjai, G. A.). Molecular orientations change reaction kinetics and mechanism: A review on catalytic alcohol oxidation in gas
phase and liquid phase on size-controlled Pt nanoparticles. *Catalysts, 8*(6), 226(2018).

22. Miller, D. M., Buettner, G. R., & Aust, S. D. Transition metals as catalysts of “autoxidation” reactions. *Free Radical Biology and Medicine, 8*(1), 95-108 (1990).

23. VELASQUEZOCHOA, J., & Cavani, F. Gas-phase oxidation of alcohols: Innovation in industrial technologies and recent developments. *Transition Metal Catalysis in Aerobic Alcohol Oxidation, 203*(2014).

24. Dong, X. Y., Gao, Z. W., Yang, K. F., Zhang, W. Q., & Xu, L. W. Nanosilver as a new generation of silver catalysts in organic transformations for efficient synthesis of fine chemicals. *Catalysis Science & Technology, 5*(5), 2554-2574(2015).

25. Wen, C., Yin, A., & Dai, W. L. Recent advances in silver-based heterogeneous catalysts for green chemistry processes. *Applied Catalysis B: Environmental, 160*, 730-741(2014).

26. Davis, S. E., Ide, M. S., & Davis, R. J. Selective oxidation of alcohols and aldehydes over supported metal nanoparticles. *Green Chemistry, 15*(1), 17-45(2013).

27. Vodyankina, O. V., Mamontov, G. V., Dutov, V. V., Kharlamova, T. S., & Salaev, M. A. Ag-containing nanomaterials in heterogeneous catalysis: Advances and Recent Trends. In *Advanced Nanomaterials for Catalysis and Energy* (pp. 143-175). Elsevier(2019).

28. Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., ... & Firsov, A. A. Electric field effect in atomically thin carbon films. *science, 306*(5696), 666-669(2004).

29. Ramanathan, T., Abdala, A. A., Stankovich, S., Dikin, D. A., Herrera-Alonso, M., Piner, R. D Brinson, L. C. Functionalized graphene sheets for polymer nanocomposites. *Nature nanotechnology, 3*(6), 327-331(2008).

30. Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhhammes, A., Jia, Y., ... & Ruoff, R. S. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *carbon, 45*(7), 1558-1565(2007).

31. Peng, H., Dang, W., Cao, J., Chen, Y., Wu, D., Zheng, W., ... & Liu, Z.. Topological insulator nanostructures for near-infrared transparent flexible electrodes. *Nature chemistry, 4*(4), 281-286(2012).

32. Karthick, R., Brindha, M., Selvaraj, M., & Ramu, S.. Stable colloidal dispersion of functionalized reduced graphene oxide in aqueous medium for transparent conductive film. *Journal of colloid and interface science, 406*, 69-74(2013).

33. Novich, B. E., & Ring, T. A.. Colloid stability of clays using photon correlation spectroscopy. *Clays and Clay minerals, 32*(5), 400-406(1984).

34. Liu, J., Davis, N. R., Liu, D. S., & Hammond, P T.. Highly transparent mixed electron and proton conducting polymer membranes. *Journal of Materials Chemistry, 22*(31), 15534-15539(2012).

35. Kim, S. H., Yu, Y., Li, Y. Z., Xu, T., & Zhi, J. F. A hybrid reduction procedure for preparing flexible transparent graphene films with improved electrical properties. *Journal of Materials Chemistry, 22*(35), 18306-18313. (2012).
36. Khrapach, I., Withers, F., Bointon, T. H., Polyushkin, D. K., Barnes, W. L., Russo, S., & Craciun, M. F. Novel highly conductive and transparent graphene-based conductors. *Advanced materials, 24*(21), 2844-2849(2012).

37. Zhu, Y., & Murali, S. W. i. Cai, X. Li, JW Suk, JR Potts and RS Ruoff. *Adv. Mater, 22* 3906-3924. (2010).

38. Hecht, D. S., Hu, L., & Irvin, G.. Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures. *Advanced materials, 23*(13), 1482-1513(2011).

39. Zheng, Q., Zhang, B., Lin, X., Shen, X., Yousefi, N., Huang, Z. D., ... & Kim, J. K.. Highly transparent and conducting ultralarge graphene oxide/single-walled carbon nanotube hybrid films produced by Langmuir–Blodgett assembly. *Journal of Materials Chemistry, 22*(48), 25072-25082(2012).

40. Kim, J., Cote, L. J., Kim, F., Yuan, W., Shull, K. R., & Huang, J. Graphene oxide sheets at interfaces. *Journal of the American Chemical Society, 132*(23), 8180-8186(2010).

41. Peng, G., Qiu, F., Ginzburg, V. V., Jasnow, D., & Balazs, A. C.. Forming supramolecular networks from nanoscale rods in binary, phase-separating mixtures. *Science, 288*(5472), 1802-1804(2000).

42. Fukushima, H. *Graphite nanoreinforcements in polymer nanocomposites*. Michigan State University (2003).

43. Kalaitzidou, K., Fukushima, H., & Drzal, L. T.. A new compounding method for exfoliated graphite–polypropylene nanocomposites with enhanced flexural properties and lower percolation threshold. *Composites Science and Technology, 67*(10), 2045-2051(2007).

44. Miloaga, D. G., Hosein, H. A. A., Misra, M., & Drzal, L. T.. Crystallization of poly (3-hydroxybutyrate) by exfoliated graphite nanoplatelets. *Journal of applied polymer science, 106*(4), 2548-2558(2007).

45. Pinto, A. M., Cabral, J., Tanaka, D. A. P., Mendes, A. M., & Magalhaes, F. D.. Effect of incorporation of graphene oxide and graphene nanoplatelets on mechanical and gas permeability properties of poly (lactic acid) films. *Polymer International, 62*(1), 33-40(2013).

46. Kulkarni, D. P., Das, D. K., & Vajjha, R. S. Application of nanofluids in heating buildings and reducing pollution. *Applied Energy, 86*(12), 2566-2573(2009).

47. Yiamsawas, T., Mahian, O., Dalkilic, A. S., Kaewnai, S., & Wongwises, S. Experimental studies on the viscosity of TiO2 and Al2O3 nanoparticles suspended in a mixture of ethylene glycol and water for high temperature applications. *Applied energy, 111*, 40-45(2013).

48. Akinlotan, O. O., & Ezenobi, U. V. A REVIEW OF VARIOUS METHODS OF SYNTHESIZING NANOPARTICLES AND THEIR APPLICATIONS. *Journal of Chemical Society of Nigeria, 45*(4) (2020).

49. Pourmortazavi, S. M., Hajimirsadeghi, S. S., Kohsari, I., Fareghi Alamdari, R., & Rahimi-Nasrabadi, M.. Determination of the optimal conditions for synthesis of silver oxalate nanorods. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology, 31*(10), 1532-1535(2008).

50. Boldyrev, V. V.. Thermal decomposition of silver oxalate. *Thermochimica acta, 388*(1-2), 63-90(2002).

51. Fiorucci, A. R., Saran, L. M., Cavalheiro, É. T. G., & Neves, E. A. Thermal stability and bonding in the silver complexes of ethylenediaminetetraacetic acid. *Thermochimica acta, 356*(1-2), 71-78 (2000).
52. Alibolandi, M., Sadeghi, F., Sazmand, S. H., Shahrokhi, S. M., Seifi, M., & Hadizadeh, F. Synthesis and self-assembly of biodegradable polyethylene glycol-poly (lactic acid) diblock copolymers as polymersomes for preparation of sustained release system of doxorubicin. International journal of pharmaceutical investigation, 5(3), 134(2015).

53. Dubey, S. P., Lahtinen, M., & Sillanpää, M. Tansy fruit mediated greener synthesis of silver and gold nanoparticles. Process Biochemistry, 45(7), 1065-1071(2010).

54. Zaheer, Z. Silver nanoparticles to self-assembled films: green synthesis and characterization. Colloids and surfaces B: Biointerfaces, 90, 48-52(2012).

**Figures**

**Figure 1**

Preparation of the catalyst composite.
Figure 2

The XRD analysis for Mn and Ag nanoparticles.
Figure 3

TEM. a – Graphene and Mn NPs; b – Ag NPS in PEG; c – Graphene inside PEG; d – Composite (PEG-NPS-Graphene).
Figure 4

TGA for a) PEHD and b) composite structure.

Figure 5

[Graph showing size distribution for Nanoparticles solution, PEG-NPs, and Composite]
Particals size analyzer for (Mn and Ag NPs, PEG-(Ag, Mn) NPs, and PEG-(Ag, Mn) NPs – Graphene colloid solution.

Figure 6

UV characterise of composite materials and their solutions.
Figure 7

Reaction mechanism estimated using CVT.
Figure 8
The pyrolysis and gasification systems set-up.

![Graph showing pyrolysis and gasification systems set-up.]

Figure 9
The optimized parameters (pressure, temperature, and time) in PEHD degradation.

![Graphs showing optimized parameters for PEHD degradation.]

(a) Char yield M3/kg vs. Catalytic Ratio %
(b) Gas yield M3/kg vs. Catalytic Ratio %
Figure 10

Product distribution using different composite loading ratio: a – pyrolysis, b – catalytic cracking.

Figure 11

Gasification process: a – without catalyst; b – using of 0.06 wt % of prepared fabricated catalyst

Figure 12

Pyrolysis process: a – without catalyst; b – using of 0.06 wt % of fabricated catalyst (Graphene /Ag-Mn NP/PEG).
Figure 13

Gas yield components distribution: a – Pyrolysis; b – Gasification.
Figure 14

Morphology of the sample of char surface as a result of thermal degradation of PEHD and composite.
Figure 15

EDX analysis of the element composition in the char sample.