Lamellar shape lead tungstate (PbWO₄) nanostructures as synergistic catalyst for peroxidase mimetic activity

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Abstract

Tungstate based nanomaterials have emerged as important class in transition metal oxide. In this study, Lead tungstate (PbWO₄) nanostructures with lamellar morphology were prepared by hydrothermal method. The synthesized materials were characterized by XRD, SEM, FTIR, DLS, BET and PL. Nitrogen adsorption-desorption measurements indicated that the surface area of the synthesized lamellar morphology was ~86.225 m² g⁻¹. The lamellar-like morphology showed enhanced peroxidase-like activity owing to the large surface area, higher substrate interaction and efficient electron transportation. The results indicated higher reaction velocity (Vmax = 13.56 × 10⁻⁹ M s⁻¹) and low Michaelis-Menten constant (km = 0.325 mM) value for nanostructures, providing evidence for higher affinity of novel structures towards the substrate and increased peroxidase-like activity. Finally, biocompatibility test was conducted by performing cytotoxicity experiments of PbWO₄ nanostructures on MTT assays.

1. Introduction

The Heme-peroxidases are most effective enzymes being employed to catalyze the oxidation of various inorganic and organic compounds by hydrogen peroxide and other compounds [1]. The main source of these enzymes is plants and numerous physiological functions. Horseradish Peroxidase (HRP) is also member of this group, found in the roots of horseradish (Armoracia rusticana) [2]. In horseradish peroxidase, particularly ‘iso-enzyme C (HRP-C)’ is one of the broadly studied peroxidase due to its availability and stability [3]. This form is most abundant from all the known iso-enzyme of horseradish peroxidase [4, 5]. HRP has been widely used in disease diagnosis, waste water treatment, medicine, bio-sensing and food processing due to their extraordinary proficiency and substrate specificity [6–8]. HRP is a series of oxidoreductases enzyme which diminish the hydrogen peroxide to water in a sense to oxidize numerous types of aromatic compounds ranging from aromatic amine to phenol [9]. The reaction pathway of HRP is relatively complex and start with initiation of heme by hydrogen peroxide which activates a couple of electrons and form compound I. This compound then reduces to compound II with the oxidation of substrate. When the compound II is formed, then enzyme move back to their resting stage and prepare to enter the next cycle of reaction. In overall reaction, two aromatic free radicals are produced against the consumption of one molecule of hydrogen peroxide. In case of waste water treatment,
HRP converts the phenolic compound to free radicals that diffuse from active center to waste water. These free radicals react with phenolic compounds present in waste water and provide compounds least soluble in water as compared to original substrate [10].

On the other hand, artificial horseradish peroxidase mimics have adjustable structures and compositions along with low cost, superior properties, facile preparation and high stability. In addition to other fields, enzymatic mimetic have been significantly affected by nanoscale materials i.e. heme-containing HRP can catalyze the oxidation of different chromogenic negatively-charged substrate such as 2, 2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), tetra methyl benzidine (TMB), and fluorogenic substrates with hydrogen peroxide, therefore, it is suitable tool in analytical and clinical chemistry, particularly in immunoassays and bio-sensing. Magnetic nanoparticles have shown tremendous response as electro-catalyst, however, zero-dimensional (carbon nanodots, ZnFe2O4, CeO2 and Au), one dimensional (V2O5) and two-dimensional (GO, organic-inorganic hybrids, C6N4 and VS2) nanomaterials have also been employed for enzyme-like activity. This opens up a new horizon in medical diagnostics and bioassay owing to novel morphologies, higher stability, tunable catalytic response, facile as well as inexpensive [11, 12].

Among the tungstate family which includes CdWO4, BaWO4, MnWO4, ZnWO4 and SrWO4, PbWO4 nanostructures are mostly utilized in high energy physics as scintillator along with low cost, superior properties, facile preparation and high stability. In addition to other properties compared to original substrate radicals react with phenolic compounds present in waste water and provide compounds least soluble in water as HRP converts the phenolic compound to free radicals that diffuse from active center to waste water. These free radicals react with phenolic compounds present in waste water and provide compounds least soluble in water as compared to original substrate [10].

2. Materials and methods

2.1. Reagents and chemicals

All the reagents in the experiment were purchased from Sigma Aldrich, bio-acros and Merck through local vendors. The chemicals were of analytical grade and purity, used without purification. Ultrapure de-ionized water (D.I.W) with resistivity of $\rho = 18$ MΩ cm obtained from Millipore-MilliQ system has been used in experiments.

2.2. Synthesis of PbWO4 with lamellar morphology

In the typical growth of PbWO4 nanostructures, briefly, 20 ml of 5 mM sodium tungstate dihydrate [Na2WO4.2H2O] was dissolved into 20 ml (1.5 mM acetic acid solution) of 15 mM lead (II) nitrate [Pb(NO3)2]. On addition of all the reagents, a milky white suspension was formed which was further vigorously stirred for 45 min to attain the complete homogenization. The pH of the suspension was kept at 10 using ammonia water and then put in the oven for hydrothermal treatment for 24 h in Teflon lined stainless steel autoclave. After completion, the obtained white precipitates were washed with deionized water and absolute ethanol, alternatively, 5 times to eliminate the surface bound impurities. The materials were dried at 80 °C for 8 h before studying the HRP-like activity [36–39].

2.3. Characterization of as-synthesized PbWO4 with lamellar morphology

The structural analysis of the as-synthesized PbWO4 nanostructures was done by using x-rays powder diffraction (XRD, Philips) using Cu Kα radiation ($\lambda = 0.15406$ nm) at 2θ ranging from 20° to 60° at room temperature. The morphology of the as-synthesized nanostructures was captured using scanning electron microscopy (Nova nano SEM, FEI). The elemental composition of the PbWO4 nanostructures was investigated by conducting Energy-Dispersive x-ray spectroscopy (EDX) using (Nova nano SEM, FEI). The surface chemistry of nanomaterials was studied using Alpha-P FTIR spectrophotometer (Bruker). Brunauer–Emmett–Teller (BET, ASAP-2020) was employed to estimate the surface area of the prepared nanostructures. Luminescence
The peroxidase-like activity of synthesized PbWO₄ nanostructures was analyzed by observing the catalytic oxidation of a negatively charged chromogenic substrate, ABTS (4.32 mM, 50 μl) in the presence of an oxidizing agent, hydrogen peroxide (H₂O₂) as co-substrate. Room temperature catalytic oxidation of ABTS was carried out using PbWO₄ nanostructures (10 μg ml⁻¹, 10–50 μl) and H₂O₂ (50 μl) in sodium acetate buffer (pH 4.3) incubated for 15 min. The microplate reader was used for the spectroscopic measurements by measuring the absorbance at 416 nm. The kinetics study of PbWO₄ nanostructures was conducted at different catalyst concentrations (10, 20, 30, 40 50 μl), while the concentrations of H₂O₂ and ABTS were kept constant. For recycling and reusing the nanostructures as peroxidase-like mimetic, the suspended nanoparticles were centrifuged and used for another reaction.

2.5. Cell culture

Human colorectal carcinoma cell line (HCT 116) was cultured in Dulbecco’s modified Eagle’s medium (DMEM, Thermo Scientific HyClone, Logan, UT, USA) supplemented with 10% Hi-FBS (Sigma-Aldrich Corp., St Louis, MO, USA), 1% Pen-strep (100 IU/ml penicillin and 100 μg ml⁻¹ streptomycin) (GIBCO, Invitrogen, NY, USA), 2mM L-glutamine and 1% non-essential amino acids (NEAAs) (GIBCO, Invitrogen, NY, USA). The HCT 116 cells were grown in cell culture flasks (tissue culture treated) (SPL Life Sciences, South Korea) and were incubated at 37 °C in a humidified atmosphere with 5% CO₂. Every 3–5 days, the adherent cells were suspended after treating with 1–2 ml of 0.25% trypsin-EDTA (GIBCO, Invitrogen, NY, USA) solution for 5–7 min at 37 °C. The cells were subcultured at 1:3 split ratio.

2.5.1. Cytotoxicity assay

Cytotoxicity activity of PbWO₄ nanostructures was determined by MTT (3-(4,5-Dimethylthiazol-2-yl)−2,5-diphenyltetrazolium bromide) assay. Briefly, HCT 116 cells were seeded in 96 well plate in 100 μl volume at a density of 0.1 × 10⁶ cells/ml. After an overnight incubation, cell culture medium was removed; PbWO₄ nanostructures were dissolved appropriately in DMEM media, sonicated and immediately added into cells. The cells were treated with PbWO₄ nanostructures at the final concentration 1–100 μg ml⁻¹. After 72 h of treatment, 10 μL MTT (12 mM) reagent was added to each well. After four hours of incubation, media was removed and 100 μL DMSO was added to each well to dissolve the end product, formazan. The absorbance was taken at 570 nm by using Synergy H1 hybrid multi-mode microplate reader (BioTek Instruments Inc., Winooski, VT, USA). Cell culture media was used as vehicle control. The results were expressed as the mean cell survival percentage. Before 10 μL MTT solution (12 mM) was added to 72 h exposure cells, their morphological changes were observed with an inverted phase contrast microscope (IMT-2; Olympus, Tokyo, Japan).

3. Results and discussion

The synthesized nanostructures are initially characterized for their structural, chemical and morphological properties. X-ray diffraction (XRD) technique is used for the analysis of crystal structure, lattice parameters, purity and phase identification of PbWO₄ nanostructures (figure 1(a)). The XRD pattern of PbWO₄ nanostructures exhibits the characteristic diffraction peaks of material indexed to stolzite tetragonal phase with space group I41/a. All the peaks are well matched with the JCPDS, Card No: 86-0843. The lattice parameters of as-synthesized PbWO₄ nanostructures are a = b = 5.4560 Å and c = 12.0200 Å with α = β = γ = 90°. XRD pattern of PbWO₄ have peaks located at 25.6°, 28.9°, 30.7°, 32.9°, 44.9°, 47.2°, 51.4°, 55.3° and 56.8° consistent with the crystal planes, (101), (112), (200), (114), (116), (132), (107), (305) and (233) respectively. XRD peaks can also provide information about preferential growth of nanostructures. The texture coefficient for all the planes of PbWO₄ has been calculated using formula given below [32].

\[
TC_{hkl} = \frac{I_{hkl}/I_{o(hkl)}}{1/N \sum \alpha (I_{hkl}/I_{o(hkl)})}
\]

Where TC_{hkl} indicates the texture coefficient, I_{hkl} represents the relative peak intensity of the sample under study, I_{o(hkl)} depicts the relative peak intensity of reference (JCPDS) pattern and N is the total number of matched with the standard data. The deviation of texture coefficient (TC_{hkl}) values from unity and highest value shows the crystals’ preferred growth orientation [33]. TC_{hkl} calculated for PbWO₄ are displayed in table 1. The maximum value of TC_{hkl} = 1.191 is associated with (200) plane. Hence, the preferential orientation of growth is along the direction of (200) plane.
X-ray Energy Dispersive Spectroscopy (EDX) is performed to estimate the chemical composition of PbWO₄ nanostructures. The result of EDX study is shown in figure 1(b). The spectrum consists of major peaks attributed to Pb, W and O, whereas C peak is due to carbon coating of the grid. This indicates that the as-synthesized product holds good purity. Quantitative analysis of the EDX spectrum provides relative concentrations of different elements present in the sample (figure 1(c)).

Figures 2(a)–(d) shows the SEM micrographs of PbWO₄ nanostructures at different magnification. Lamellar-like morphology can be observed in the images. This one dimensional lamellar-like morphology presents the enhanced surface activity feasible for the catalytic application. Low magnification images confirm the formation of high density of nanostructures, whereas, aggregation at higher magnification can be explained on basis of inter-particle interactions during hydrothermal process. The average diameter of one-dimensional lamellar nanostructures was in the range of 30 to 40 nm.

FTIR is used to study the chemical interatomic compatibility, catalyst surface properties and effect of temperature on vibrational modes of chemical groups in nanomaterials. FTIR spectrum of PbWO₄ nanostructures is shown in figure 3(a). Yu et al 2015 [40] described that characteristic absorption bands ranging from 700 to 900 cm⁻¹ can be attributed to W-O bonds and vibrational stretching of tetrahedral WO₄. While, band located at 1425 cm⁻¹ can be ascribed the OH bending modes. A strong band with highest intensity is observed at 743.70 cm⁻¹ which belongs to ν3 mode of WO₄²⁻ anions. Shoulder observed at 802 cm⁻¹ is linked ν3 (W–O) asymmetric stretching in WO₄ [41]. The broadness of the band is believed to be linked with the nano-type nature of PbWO₄ crystals. During catalysis (OH) radicals are usually dissociated by discharging photogenerated holes (h⁺) to form •OH, potentially improve catalytic activity of materials [42].

Photoluminescence (PL) spectrum is taken to explore the optical properties of lamellar shaped PbWO₄ at an excitation wavelength of 300 nm, as shown in figure 3(b). PL spectrum shows a strong and broad emission peak at 502.62 nm (2.47 eV), attributed to near band edge emission. The calculated value of band gap for PbWO₄ is blue shifted in comparison to typical value i.e. 4.5 eV. However, band gap up to 2.96 eV has been reported for...
PbWO$_4$ nanomaterials [21]. It is already evident from the literature that morphology of the PbWO$_4$ influenced its optical properties. This reduction in band gap can be associated with the specific lamellar morphology of the nanostructures as Talebi, 2016[26] observed band gap value of 3 eV for rod like PbWO$_4$ nanostructures. Another factor that can affect the optical properties, is the inhomogeneous distribution of the samples as well as surface defect distribution which can vary the overlaps of the transitions and causes shifting in absorption bands [43–45]. The blue emission level is ascribed to lead and tungstate, owing to regular lattice contributions, whereas, green emission originates due to oxygen associated lattice defects [44, 46]. The slight red shift in PL wavelength is attributed to somewhat large size nanostructured material lying beyond the boundary of quantum confinement regime. It is presumed that PbWO$_4$ possess extensive defects enabling it to exhibit intense PL band

Figure 2. SEM images of the as-synthesized PbWO$_4$ with lamellar morphology captured at different magnification.

Figure 3. (a) Fourier Transform Infrared (FTIR) (b) photoluminescence spectrum of as-synthesized lamellar PbWO$_4$ nanostructures.
emission and indicating dependency of photoluminescence emission band of PbWO$_4$ on the crystal structure, their crystallinity and structural defects [47].

For the assessment of specific surface area of PbWO$_4$ nanostructures, the isotherm linear plot of nitrogen adsorption-desorption was drawn. Figure 4 shows the nitrogen physical adsorption desorption isotherm linear plot of PbWO$_4$ nanostructures. Barrett–Joyner–Halenda (BJH) method is employed to quantify the pore size from desorption isotherm plot. The BET surface area, single point area (at $P/P_0 = 0.200561427$), Langmuir area and pore width are found to be 86.225 m$^2$ g$^{-1}$, 83.1400 m$^2$ g$^{-1}$, 119.9620 m$^2$ g$^{-1}$ and 9.74312 nm respectively.

3.1. Peroxidase-like activity of lamellar shaped PbWO$_4$ nanostructures

PbWO$_4$ nanostructures quickly catalyze the chromogenic substrate ABTS by oxidation, producing greenish color for the substrate in the presence of H$_2$O$_2$ as shown in figure 5(A)(inset). Although H$_2$O$_2$ is used as catalyst to initiate the invisible oxidation of organic substrates, it is hypothesized that heterogeneous catalyst accelerates the electron-transfer process by the decomposition of H$_2$O$_2$ to produce sufficient number of hydroxyl radical (·OH) and oxygen as reactive species [48]. The colorimetric reaction schematic is shown in the figure 7, indicating the peroxidase reaction mechanism. The stability and dispersity of PbWO$_4$ were studied by using DLS (dynamic light scattering). The nanostructures are highly dispersible in aqueous media and exhibit zeta potential of +67.2 mV (figure S1 is available online at stacks.iop.org/MRX/7/015520/mmedia).
The maximum absorbance for the catalytic oxidation of ABTS using lamellar morphology of PbWO₄ nanostructures is obtained at 416 nm, representing the cation radical formation of ABTS by one-electron oxidation \[49\]. PbWO₄ and H₂O₂ cannot individually oxidize ABTS; however, complete catalytic reaction can only take place by the interaction between lamellar shaped PbWO₄, H₂O₂ and ABTS. ABTS has high affinity due to di-sulfonic acid groups and PbWO₄ morphology have positive surface charge. The catalytic oxidation is increased because of higher electrostatic interaction between catalyst (PbWO₄) and substrate (ABTS). Room temperature peroxidase like catalytic activity of lamellar shaped PbWO₄ nanostructures is estimated by optimizing the pH at 4.3. ABTS is a chromogenic colorless substrate that gives a green color after getting oxidized in the presence of hydrogen peroxide and PbWO₄ nanostructures. The absorbance of greenish product is observed at 416 nm (figure 5(a)), whereas the nanoparticles dependence on absorption has been illustrated in figure 5(b). For the comparison of relative rate of greenish product development, the oxidation is checked with respect to time. Figures 6(a) and (b) is an illustration of kinetics assay.
The kinetic assays are carried out for the different concentrations of PbWO₄ nanostructures, to calculate the $K_m$ (Michaelis–Menten constant) value as given in table 2. The lower the $K_m$ value, higher will be the affinity for catalyst concentration. The lamellar-like morphology of as-synthesized PbWO₄ has an extraordinary effect on the peroxidase-like catalytic activity. These results indicate the significance of nanostructures for the catalytic oxidation properties. Therefore, the highest catalytic activity of PbWO₄ nanostructures would be ascribed to the size and novel lamellar morphology, however, the basic principle of peroxidase-like activity is vague.

**Biocompatibility Test (Cytotoxicity studies)**
MTT assay is a broadly recognized, non-radioactive, calorimetric based assay. It is derived from tetrazolium salt which converts into purple formazan complex due to enzyme in mitochondrial dehydrogenases [54]. The

![Figure 8. Effect of NPs on the viability of HCT 116 cells. A) Cell morphology of HCT 116 was monitored by inverted microscopy. The cells were exposed to NPs for 72 h. Cell culture media was used as vehicle control. B) The cell viability by MTT assay. The results were expressed as the mean cell survival (%) compared to vehicle control.](image-url)
viability of HCT 116 cell lines was investigated using MTT assay for PbWO4 nanostructures at different dose concentrations i.e. 1 \( \mu \text{g} \text{ml}^{-1} \), 10 \( \mu \text{g} \text{ml}^{-1} \), 25 \( \mu \text{g} \text{ml}^{-1} \), 50 \( \mu \text{g} \text{ml}^{-1} \), 75 \( \mu \text{g} \text{ml}^{-1} \), 100 \( \mu \text{g} \text{ml}^{-1} \) for 72 h. Cell culture media was used as control vehicle. There was least viability and cell proliferation of HCT 116 cell lines observed up to 75 \( \mu \text{g} \text{ml}^{-1} \) dose. Increased viability and cell proliferation were witnessed for 100 \( \mu \text{g} \text{ml}^{-1} \) (figure 8(a)). Morphological character of treated and control cell lines were illustrated by inverted microscopy. Cell viability for different concentrations of PbWO4 nanoparticles is presented in figure 8(b). The cell viability of the sample as compare to control (cell culture media) showed no significant sign of cytotoxicity at different colloidal concentrations for 72 h except at 100 \( \mu \text{g} \text{ml}^{-1} \). At higher concentration level i.e. 100 \( \mu \text{g} \text{ml}^{-1} \), there was increase in cell activity observed. There are different parameters such as concentration, method of preparation and structure that can affect the cell viability of MTT assay. These results showed better cell viability of PbWO4 without inducing any toxicity which confirmed the biocompatibility of synthesized nanomaterials. This may be attributed to the inertness of the nanomaterials in the cultured media [55].

4. Conclusion

Lamellar shaped lead tungstate (PbWO4) nanostructures have been successfully synthesized using hydrothermal strategy, which exhibited stable horseradish peroxidase (HRP)-like activity at room temperature. The peroxidase-like activity of the cationic PbWO4 nanostructures was studied using ‘ABTS’ as a chromogenic substrate in the sodium acetate buffer at pH 4.3 in the presence of \( \text{H}_2\text{O}_2 \) as the co-substrate. XRD, SEM, EDX, PL, FTIR, BET and DLS were used for elaborative characterization of the as-synthesized nanostructures. The lamellar-like structures showed enhanced peroxidase-like activity owing to the large surface area, higher substrate interactions and efficient electron transportation. PbWO4 nanostructures have higher reaction velocity \( (V_{\text{max}} = 13.56 \times 10^{-8} \text{ M s}^{-1}) \) and low \( (km = 0.325 \text{ mM}) \) value, providing evidence for higher affinity of novel structures towards the substrate and increased peroxidase-like activity.

Conflict of interest

The authors have no conflict of interest to declare.

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