One Step Synthesis of a Gold/Ordered Mesoporous Carbon Composite Using a Hard Template Method for Electrocatalytic Oxidation of Methanol and Colorimetric Determination of Glutathione

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Supporting Information

ABSTRACT: Ordered mesoporous carbon-supported gold nanoparticles (Au/OMC) have been fabricated in one step through a hard template method using gold nanoparticle-intercalated mesoporous silica (GMS) to explore two different catalytic properties, for example, electrocatalytic oxidation of methanol and colorimetric determination of glutathione (GSH). The catalytically inert but conducting nature of mesoporous carbon (OMC) and promising catalytic activity of gold nanoparticles (AuNPs) has inspired us to synthesize Au/OMC. The as-prepared Au/OMC catalyst was characterized by powder X-ray diffraction, N₂ adsorption−desorption, scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray analysis-elemental mapping, and X-ray photoelectron spectroscopy. The characterization results indicate that AuNPs are uniformly distributed on the surface of OMC. The conducting-OMC framework with a high surface area of Au/OMC provides superior transport of electrons through the porous surface of carbon matrix and resulted in its high efficiency and stability as an electrocatalyst for the oxidation of methanol in comparison to CMK-3, SBA-15, and GMS in alkaline medium. The efficiency of Au/OMC toward methanol oxidation in alkaline medium is much higher in comparison to that in acidic medium. The lower value of Iₓ/Iₒ in the acidic medium in comparison to that in the alkaline medium clearly indicates that the oxidation process with Au/OMC as a catalyst is much more superior in alkaline medium with better tolerance toward the accumulation of intermediate CO species on the active surface area. Furthermore, the Au/OMC catalyst is successfully utilized for the detection and quantification of GSH spectrophotometrically with a limit of detection value of 0.604 nM.

INTRODUCTION

Carbon-based materials such as fullerenes, carbon nanotubes, and graphene have found a pivotal role in the field of nanotechnology owing to their unique properties and flexibility. In the recent past, ordered mesoporous carbon (OMC) has also attracted considerable attention. The diverse physiochemical properties of OMCs for example hydrophobicity of their surfaces, high corrosion resistance, mechanical stability, highly active porous surface area, large pore volume, interconnected network of ion diffusion channels, good conductivity, thermal stability, chemical inertness, easy handling, and low cost of manufacturing have largely increased the domain of their applications in the field of energy conversion, chemical catalysis, biomedicine, drug delivery, sensors, and solar cell fabrication. Amongst different strategies for the synthesis of OMCs, the template strategy is the most popular method and can be classified into two major sections: hard template approach using mesoporous silica SiO₂, CaCO₃, and so forth and soft template approach utilizing self-assembly of the surfactant micelles to determine the carbon shape. Because of better control of the morphology of the target product, we have chosen the hard template strategy for the one-step synthesis of ordered mesoporous carbon-supported gold nanoparticle (Au/OMC) catalyst. So far, only few gold nanoparticle (AuNP)-supported mesoporous carbon (Au/OMC) synthesized by the hard template method has been reported in the literature using a two-step process, where at first the mesoporous carbon
framework was prepared via the hard template synthetic strategy followed by wet impregnation of the OMC framework with Au(III) and reduction of Au(III) to Au(0). Tuel and his co-workers also reported AuNP containing CMK-3 (AuNPs/CMK-3), where Au$_x$SBA-15 was first prepared through wet impregnation of SBA-15 with Au(III) followed by reduction to Au(0) with NaBH$_4$, where AuNPs were grown inside the pore. Consequently, the hard template procedure has been utilized using Au$_x$SBA-15 to get AuNPs/CMK-3. Here in this work, we have reported the synthesis of Au/OMC involving a one-step hard template strategy without using any reducing agent.

In the present worldwide scenario, the extensive consumption and exhaustion of fossil fuels have led to develop an alternative route to mitigate the fuel combustion and hence reduce global warming. Direct methanol fuel cell has drawn much attention as an alternative source of power for portable and vehicular applications. Thus, methanol for its simplicity, versatility, and high energy density, next to hydrogen, can be used as a source of fuel and has thus gained much popularity for its energy conversion efficiency along with low pollution emissions. Now to utilize it as a fuel source, the situation demands the fabrication of an electrocatalyst which can effectively oxidize methanol. Use of noble metals like platinum and palladium on a carbon template for the electro-oxidation of methanol is widely exploited. However, Pt- or Pd-based catalysts often exhibit “catalyst poisoning effects” due to the strong adsorption of CO produced in intermediate steps. In order to overcome this difficulty, gold is often used as an alternative to Pt or Pd, and gold-based catalysts have emerged to be an active catalyst toward oxidation reactions. Thus, utilizing the versatility of mesoporous carbon materials, and keeping all the above facts in our mind, we have synthesized a Au/OMC catalyst where mesoporous carbon is used as a framework and the AuNPs are anchored on the surface of OMC. The support and conducting property that OMC provides to the AuNPs make the material stable and enhance the effectiveness of Au/OMC to effectively catalyze the methanol oxidation reaction (MOR) in comparison to CMK-3, SBA-15, and GMS. Thus, Au/OMC proves that it can be used as an efficient electrocatalyst with promising roles for different fuel cell applications in the future.

Besides the dual effect of diverse morphology of mesoporous carbon and catalytic features of Au, Au/OMC shows a very good peroxidase-like activity which is further utilized for the detection of glutathione (GSH). GSH (L-γ-glutamyl-L-cysteinyl-glycine) is the most abundant intracellular non-protein thiol. Because GSH has different vital multitasking functions within our body like maintaining immunity, detoxification of peroxides and free radicals (antioxidant property), and regulations of protein function and cell growth; therefore, imbalance of GSH within our body can cause serious health hazards like cellular damage, liver damage, and even cancer. Keeping these in mind, we have herein reported a simple colorimetric assay to detect and quantify the amount of GSH present.

Thus in the present work, we have successfully synthesized Au/OMC in a one-step process, where in situ reduction of Au(III) to Au(0) occurs without using any reducing agent thereby making it environment friendly. The spherical Au NPs with an average size of 10 ± 0.38 nm are homogeneously dispersed on the surface of OMC. The as-prepared Au/OMC catalyst acts as an active electrocatalyst for the oxidation of methanol as well as the colorimetric detection of GSH in the nanomolar range.

**RESULTS AND DISCUSSION**

**Synthesis and Characterizations of Au/OMC.** The Au/OMC material has been synthesized using mesoporous silica with AuNPs intercalated inside the pore walls (GMS) as hard-template. However, here the synthesis of GMS involves a one-pot modified sol–gel preparation without the use of any reducing agents. The addition of bis[3-(triethoxysilyl)propyl]-

Scheme 1. Synthesis of Au/OMC Using AuNPs Intercalated Mesoporous Silica (GMS) as a Hard Template

Figure 1. (a) Wide-angle and (b) low angle powder XRD patterns of Au/OMC composite and pure OMC.

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tetrasulfide (TESPTS) and HAuCl₄ during the formation of SBA-15 integrates Au into the wall-framework of SBA-15 (Scheme 1). Impregnation of as-prepared GMS with glucose as a carbon source followed by carbonization and subsequent removal of the silica template with hydrofluoric acid (HF) produced Au/OMC (Scheme 1). The unloaded mesoporous carbon material (CMK-3) was also prepared using pure SBA-15.

The wide-angle powder X-ray diffraction (XRD) pattern of Au/OMC is shown in Figure 1a. The presence of characteristic peaks of AuNPs in wide-angle XRD of the Au/OMC confirms the presence of the crystalline Au phase. The diffraction pattern matches quite well with the standard diffraction data of the AuNPs with the face-centered cubic lattice (Fm3m space group) and cell parameter 4.078 Å (JCPDS no. 04-0784). The XRD pattern (Figure 1a) shows distinct diffraction peaks at 2θ = 38.53°, 44.74°, 64.9°, 77.94°, and 82.05° corresponding to the lattice planes (111), (200), (220), (311), and (222) of AuNPs, respectively. The broad peak appearing at 2θ = 22.8° can be indexed to the lattice plane (002) of the mesoporous carbon support. The low-angle XRD patterns of Au/OMC and CMK-3 are displayed in Figure 1b.

Both the samples exhibit an intense diffraction peak for the (100) plane which indicates the formation of an ordered 2D hexagonal mesostructure. Additionally, broad ill-defined less intense superimposed peaks for (110) and (200) planes are observed for CMK-3 although these low intense peaks are not quite clear in Au/OMC.

The nitrogen adsorption–desorption isotherms and pore size distribution determined for Au/OMC and CMK-3 are displayed in Figure 2. Both the materials exhibited type IV adsorption–desorption isotherms (Figure 2a), which are characteristic of mesoporous materials. A relatively high surface area and pore volume of 770 m² g⁻¹ and 0.984 cm³ g⁻¹, respectively, were observed for the unloaded mesoporous carbon CMK-3. Whereas, the Brunauer–Emmett–Teller (BET) surface area and pore volume of the as-prepared Au/OMC sample were found to be 600 m² g⁻¹ and 0.5 cm³ g⁻¹, respectively, in Au/OMC. The reduced surface area and pore volume for Au/OMC may be attributed to the loading of AuNPs on the surface of the mesoporous carbon matrix. The pore size distribution plots of these samples were estimated by using the nonlocal density functional theory (NLDFT) model (Figure 2b). A narrow pore size distribution centered around 5.0 nm was found for both Au/OMC and CMK-3 which further indicates that the AuNPs have been deposited on the surface of OMC.

The morphology of Au/OMC, size of the AuNPs, and their dispersion over the mesoporous carbon framework were analyzed by field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and energy-dispersive X-ray (EDX) analysis elemental mapping.

Figure 2. Physisorption isotherms (a) and corresponding NLDFT pore size distributions (b) of Au/OMC and CMK-3.

Figure 3. (a) SEM image, (b) TEM image, (c) Au particle size distribution, and (d–f) TEM–EDS elemental mapping of Au/OMC.
The synthesized OMC exhibits a “noodle” like or spherical morphology in Au/OMC which is different from CMK-3 as shown in the FESEM image (Figure 3a). The TEM image of Au/OMC is shown in Figure 3b, where spherical AuNPs with an average size of 10 ± 0.40 nm (Figure 3c) are seen to be evenly distributed on the surface of the OMC. From the high-angle annular dark field-scanning electron micrograph of Au/OMC (Figure S1), it could be clearly observed that spherical AuNPs with the size in the range from 5 to 14 nm are uniformly distributed on the surface of the OMC support. Gold particles are probably capped by the C=O and C–OH groups formed on the surface of OMC. A small portion of the AuNPs has also grown inside the pore channels as evident from the reduced surface area in Au/OMC than CMK-3. The SEM–EDX (Figure S2) also clearly shows the elemental distribution of AuNPs on the carbon framework. Besides, both SEM–energy-dispersive X-ray spectroscopy (EDS) particle mapping (Figure S3) and TEM–EDS particle mapping analysis (Figure 3d–f), demonstrates that AuNPs are loaded as a homogenous dispersion on mesoporous carbon.

The surface composition and electronic structure of Au/OMC were studied by X-ray photoelectron spectroscopy (XPS) analysis. A wide XPS scan of the sample (Figure 4a) shows the presence of Au, C, and O. The peaks at around 284.8 and 532.1 eV in the survey spectrum clearly confirm that the chemical components are C 1s and O 1s, respectively. The binding energies observed were calibrated using a carbonaceous C 1s line (284.6 eV) as a reference. A small peak binding energies observed were calibrated using a carbonaceous C 1s line (284.6 eV) as a reference. A small peak corresponding to Au 4f is also observed at 86 eV in the survey spectrum. The enlarged XPS scan of Au 4f (Figure 4b) actually shows two peaks appearing at 84.25 and 87.90 eV which can be corresponding to Au 4f is also observed at 86 eV in the survey spectrum. The enlarged XPS scan of Au 4f (Figure 4b) actually shows two peaks appearing at 84.25 and 87.90 eV which can be assigned to Au 4f(7/2) and Au 4f(5/2), respectively, thereby indicating the presence of Au(0). Also from the enlarged C 1s spectrum (Figure 4c), a major characteristic peak (C–C) for a graphitic carbon framework is observed at 284.6 eV. Besides this, a peak with reduced intensity at a binding energy of 286.1 eV has appeared due to C–O bonds as expected for CMK-3 type of materials.29 The broadness of the peak appeared for C–O bonds owing to the presence of both C=O and C–OH as reported previously.29

Electrochemical Performance of Methanol Oxidation.
The MOR efficiency of Au/OMC was evaluated by cyclic voltammetry (CV) analysis. A comparative study for the MOR by the synthesized catalyst along with CMK-3, GMS, and SBA-15 was performed both in acidic and alkaline media. Figure 5 shows the cyclic voltammograms of Au/OMC, CMK-3, GMS, and SBA-15 toward the oxidation of 1 M methanol in 1 M H2SO4 at a scan rate of 50 mV s−1. A pair of peaks at 0.339 V (anodic) and 0.27 V (cathodic) is observed in the cyclic voltammogram (Figure S4) of Au/OMC in 1 M H2SO4 without methanol. The peaks observed for Au/OMC are different from the characteristic redox peaks reported for gold-based catalysts in acidic medium. This may be due to the very low concentration of gold on mesoporous carbon and the conducting nature of the carbon matrix.

For Au/OMC, the forward anodic peak (Iφ) at 0.755 V is due to the oxidation of methanol whereas during the backward scan, the peak (Ib) observed at 0.459 V is due to the oxidation of the adsorbed CO which is generated due to the incomplete oxidation of methanol during the forward anodic scan.19,30 It can be noted that the peak current density is the highest for Au/OMC catalyst in comparison to the other materials tested. The peak current densities of Au/OMC, CMK-3, GMS, and SBA-15 in acidic and alkaline medium are given in Figure S5 (Supporting Information).

Next, MOR potentials of Au/OMC, CMK-3, GMS, and SBA-15 were examined and compared in 1 M aqueous NaOH solution containing 1 M methanol. In alkaline medium, the redox process for the electro-oxidation of methanol exhibited by Au/OMC occurs at a much lower potential than that in the acid medium as shown in Figure 6. A pair of distinct anodic and cathodic peaks is detected at −0.149 and −0.258 V. Because the Iφ value is directly related to the oxidation of methanol, the parameter (Iφ/Ib) has much importance. The lower value of Iφ/Ib in alkaline medium in comparison to that in the alkaline medium (Table 1) indicates that the oxidation process is much more superior in alkaline medium with less accumulation of intermediate CO species on the active surface area19,31 of the catalyst and a better tolerance of Au/OMC in alkaline medium. The electrochemical results reveal that the
An important factor because OH advantage of using the alkaline medium over acidic medium is "oxidation precursors are generated by the reaction of OH strongly depends on pre-oxidation precursors." These pre-anodic oxidation process. Kwon et al. recently has shown oxides. The oxides are associated with the reactivation of the Au surface. The surface of gold must consume enough Au in alkaline medium. The Au that does not lead to any appreciable oxidation activity like that in acidic medium.23 The Au−O species which are produced after MOR are again reduced to Au(0) in a backward scan, thereby generating the active sites so that the oxidation of MeOH occurs on clean Au surfaces. Moreover, MOR in alkaline medium occurs at a low onset potential with less CO poisoning effects than that in acidic medium. Plausible pathways for MOR both in acid and alkaline medium are given in Scheme S1 (Supporting Information). As shown in eq S10 (Scheme S1), strongly adsorbed CO species is generated in acidic medium which poisons the catalyst. Moreover, because H+ is produced during MOR in acidic medium, the increasing acid concentration decreases the progress of the reaction as per the La Chatelier’s principle. Thus, it can be concluded that the reaction in alkaline medium is more feasible than in acidic.

**Electro-Oxidation of Methanol by Au/OMC in Alkaline Medium.** The most important aspect of MOR in alkaline medium using gold or other noble metals as an electrocatalyst is that the presence of base makes noble metal-based catalysts active toward MOR without using small particles or oxidic support. As reported earlier, the MOR by a gold-based catalyst in alkaline medium primarily proceeds by two independent pathways at different potential regions. Methanol oxidizes to formates at a lower potential via a 4e− exchange mechanism as shown below.32,35

\[
\text{CH}_3\text{OH} + 5\text{OH}^- = \text{HCOO}^- + 4\text{H}_2\text{O} + 4e^-
\]

However, methanol is oxidized to carbonate at a higher potential via a 6e− transfer pathway

\[
\text{CH}_3\text{OH} + 8\text{OH}^- = \text{CO}_3^{2-} + 6\text{H}_2\text{O} + 6e^-
\]

The methanol oxidation in alkaline medium by Au/OMC occurs at a low potential region, prior to the surface oxidation of Au/OMC, and it starts from −0.4 V (Figure 7). The gradual increase of current in this range may be due to the chemical adsorption of OH− on the surface of the catalyst followed by pre-oxidation of the Au surface layer, that is, Au−OHads(1−)layer generation takes place.32 In this potential window, the oxidation of both the methanol and Au surface takes place. The current reaches its maxima at −0.149 V after which the current diminishes gradually due to the Au oxide monolayer formation (Au−O) for which the methanol electro-oxidation process slows down. At a more positive potential greater than 0.2 V, an increase in the anodic current is noted which may be interpreted as the reactivation of the anodic oxidation process by Au−O.32 During the reverse potential scan, a cathodic peak at −0.258 V is observed. The peak may arise due to the removal of the Au−O monolayer formed during the forward oxidation scan, as a result of which Au−OHads(1−)species are again regenerated which reinitiate the oxidation of methanol.

The oxide-mediated reaction pathway in the electro-oxidation of methanol is mediated by a six-electron process at a higher potential, and the reaction products are carbonates as depicted in eq 3. However, Au catalysts at a lower potential window provide different reaction pathways at which the reaction intermediates may be further oxidized, which helps to reduce catalyst poisoning. Another reason for which Au catalysts are also considered to be highly advantageous is their ability to reduce the poisoning of COads. The intermediate CO formed due to the side reaction of methanol oxidation blocks

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**Table 1. Different Electrochemical Parameters of Au/OMC for MOR in Acidic and Alkaline Medium**

| Medium | Onset Potential (V) | Forward Anodic Current (I/μA) | Backward Cathodic Current (I/μA) | L/Ia |
|--------|---------------------|-----------------------------|---------------------------------|------|
| Acidic | 0.431               | 48.6 (at 0.755 V)            | 64.87 (at 0.459 V)              | 0.749|
| Alkaline | −0.396             | 35.7 (at −0.149 V)           | 8.6 (at −0.258 V)              | 4.151|

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**Figure 6.** Cyclic voltammetric responses of Au/OMC, CMK-3, GMS, and SBA-15 for the electro-oxidation of 1 M methanol in 1 M aqueous NaOH saturated with N2 at a scan rate of 50 mV s−1.

**Figure 7.** Cyclic voltammetric responses of Au/OMC in a 1 M nitrogen-saturated NaOH solution in aqueous medium with and without 1 M methanol at a scan rate of 50 mV s−1.
the active reaction sites of the catalysts and thereby results in poisoning of the catalyst. Au catalysts in alkaline medium can effectively oxidize the adsorbed CO which minimizes the poisoning effect (eq 4).

$$\text{CO}_{\text{ads}} + \text{Au} - \text{OH}_{\text{ads}} \rightarrow \text{OH} - \text{Au} - \text{CO} \rightarrow \text{Au} - \text{COOH}$$
$$\rightarrow \text{Au} + \text{CO}_2 + \text{H}_2\text{O}$$

Besides this, the large porous framework of carbon in the Au/OMC catalyst with the Au NPs anchored on the surface of carbon provides accessible routes for the diffusion of charge and electrolyte which may also favor the electro-oxidation process. The effects of change of the scan rates during the methanol oxidation process are shown in Figure 8a. It is clearly seen that the peak current increases with the increase of the scan rate and the peak current linearly increases with the square root of the scan rate (Figure 8b) which indicates that the electron transfer is reversible in terms of the diffusion layer thickness.

The electrochemical active surface area (ECSA) of the Au/OMC catalyst is determined using the following equations

$$\text{Charge (Q)} = \frac{\text{area}}{\text{scan rate}}$$

$$\text{ECSA} = \frac{Q}{390 \mu \text{C cm}^{-2}}$$

where a value of 390 $\mu \text{C cm}^{-2}$ has been suggested for polycrystalline gold. As per the equations, the ECSA of the Au/OMC catalyst is $3.216 \text{ cm}^2$. This is a very large active surface area in comparison to its SBA-15 counterpart.

**Electro-Oxidation Response of Other Alcohols by Au/OMC in Alkaline Medium.** Next, we examined the electro-oxidation of other alcohols like ethanol and isopropanol. The cyclic voltammograms (Figure 9) of ethanol and isopropanol show that Au/OMC can also catalyze electro-oxidation of these alcohols in alkaline medium. From Figure 9, it is clearly seen that the anodic peak current is maximum for isopropanol followed by ethanol and methanol. The highly active porous surface area of OMC along with the homogeneous dispersion of AuNPs provide a faster mass-transfer route which increases the electroactivity of isopropanol despite having higher molecular mass and low polarity. Figure S6 (Supporting Information) shows the electrochemical impedance spectroscopy of Au/OMC measured and compared with CMK-3 in the frequency range of 1 Hz to 1000 kHz in 1 M NaOH and MeOH solution. The low-frequency range of the hemispherical arc indicates the total resistance of charge carriers and the other is that the minimum value of $R_s$ indicates that the material experiences lower Ohmic resistance at the electrode–electrolyte interface. The resistive parameters are listed in Table S1 in Supporting Information. It can be seen from the data that Au/OMC has lower $R_s$ (24.77 $\Omega$) and lower $R_{CT}$ (45.07 $\Omega$) values in comparison to CMK-3 indicating that the charge-transfer is better in Au/OMC than CMK-3.

The stability of the Au/OMC catalyst has been assessed by the chronoamperometric and repetitive cyclic voltammetric analysis for five consecutive cycles in alkaline medium. Figure 10a depicts the chronoamperometric stability of the catalyst from where it is clearly seen that Au/OMC attains good stability in comparison to both CMK-3 and GMS. The slower initial decay of current for Au/OMC in comparison to other catalysts signifies the fact that Au/OMC has the highest tolerance to carbonaceous species, such as CO, produced during methanol oxidation in alkaline medium. The repetitive cycling durability in basic medium (Figure 10b) shows that the current remains almost the same, which indicates the stability of the material during the electro-oxidation of methanol in basic medium.

**Peroxidase-like Activity of Au/OMC.** The peroxidase-like activity of Au/OMC was investigated through the catalytic oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB), a peroxidase substrate, in the presence of H$_2$O$_2$ and the Au/OMC catalyst. The catalytic reaction was monitored spectrophotometrically at room temperature from the increase of
absorbance intensity of a peak generated at 653 nm. During the reaction, due to oxidation of TMB in the presence of peroxide and the catalyst, the color change from colorless to blue is visible with the generation of the peak at 653 nm. The phenomenon shows that Au/OMC in the presence of peroxide, mimic the peroxidase-like activity as shown by horseradish peroxidase (HRP) enzyme. The highest absorbance at 653 nm is observed for the reaction where all three components—Au/OMC, H₂O₂, and TMB are present in the system. Controlled experiments with TMB−H₂O₂ showed that the absorbance at 653 nm is substantially lower than the Au/OMC−TMB−H₂O₂ system within the same period of time, and Au/OMC−TMB had the least absorbance at 653 nm (Figure 11). The observations indicate that for the highest catalytic activity, the presence of Au/OMC, H₂O₂, and TMB is very important. It is also evident from Figure 11 that Au/OMC exhibited better activity than both CMK-3 and GMS. Temperature and pH also play a vital role in the peroxidase activity. The oxidation of TMB in the presence of H₂O₂ and the catalyst is strongly dependent on pH, as shown in Scheme S2 (Supporting Information). As shown in Figure S7, the blue color of the oxidized TMB was generated only at pH 4.0. At a pH lower than 4.0, a yellow color (Figure S7) is observed due to the formation of diimine species (Scheme S2), whereas at higher pH no color change is observed. The temperature also plays a vital role during the generation of the charge-transfer complex (Scheme S2), which is blue in color. Moreover, during the oxidation, a catalyst–substrate complex formed and the formation depends on the temperature. The standardization of this catalysis at pH range 2−7 and temperature range 20−60 °C shows that the highest activity is shown at pH 4 and temperature 40 °C (Figure S8, Supporting Information).

**Steady State Kinetic Response of the Au/OMC Catalyst.** The quantification of the peroxidase-like activity of Au/OMC, in comparison to HRP, is analyzed by steady-state kinetics for the oxidation of TMB and H₂O₂ by varying the concentrations of either of the substrates and keeping the concentration of others constant (Figure 12). The important kinetic parameters like Kₘ (Michaelis–Menten constant) and Vₘₐₓ (maximum rate of conversion) are obtained by plotting V₀ against S₀ from steady-state kinetics and fitting with the Michaelis–Menten equation. The double reciprocal Lineweaver–Burk plot is obtained by plotting 1/V₀ against 1/S₀. The binding affinity between the substrate and the enzyme is evaluated from Kₘ. Smaller the Kₘ value, higher will be the
enzyme affinity for its substrate, and the parameter \( V_{\text{max}} \) directly measures the enzymatic catalytic activity. The calculated values of \( K_m \) and \( V_{\text{max}} \) are given in Table 2. From the table tabulated in Table 2 it is seen that the \( K_m \) values of Au/OMC with either peroxide or TMB as the substrate is very much lower than that of natural enzyme HRP indicating a much higher affinity of Au/OMC than HRP toward the substrates. Thus, there is a clear indication that Au/OMC can be considered as an excellent peroxidase mimicking enzyme.

The peroxidase-like activity of Au/OMC can also be conducted with ortho-phenylenediamine (OPD) as a peroxidase substrate in addition to TMB by monitoring a gradual change in absorbance at 448 nm. The peak at 448 nm is developed during the reaction of OPD with \( \text{H}_2\text{O}_2 \) in the presence of the catalyst with a visible change in color from colorless to yellowish-orange (Figure 13).

![Figure 13. Absorbance spectra and visual change in color of TMB and OPD with the generation of peaks at 653 and 448 nm, respectively, upon reaction with peroxide in the presence of Au/OMC catalyst.](image)

It is assumed that the \( \text{OH}^* \) radical generated because of the catalytic decomposition of \( \text{H}_2\text{O}_2 \) catalyzed by the nanoenzyme, oxidizes the substrate as shown in the case of the Fenton Haber–Weiss reaction occurring in biological cells. To prove the generation of the \( \text{OH}^* \) radical, a simple experiment has been performed using terephthalic acid (TPA) as a fluorescent probe. TPA can selectively capture the \( \text{OH}^* \) radical generated and forms 2-hydroxyterephthalic acid which is a highly fluorescent moiety with an emission peak at 439 nm. The generation of an emission peak at 439 nm (Figure 14) with a gradual increase in peak intensity with time in the presence of Au/OMC and \( \text{H}_2\text{O}_2 \) clearly clarifies that \( \text{OH}^* \) radicals are generated in the course of the reaction due to the decomposition of peroxide and that Au/OMC mimics peroxidase-like activity following the Fenton Haber–Weiss reaction model.

**Spectrophotometric Detection and Estimation of GSH Using the Au/OMC Catalyst.** Utilizing peroxidase-like activity of Au/OMC, a simple colorimetric assay has been developed for the detection of GSH. A visible chromogenic transition from blue to colorless is observed when a specific amount of GSH has been spiked in the TMB, \( \text{H}_2\text{O}_2 \) and Au/OMC system and this can be utilized to detect and quantify the amount of GSH present in a sample. With the gradual increase in the concentration of GSH from 0 to 300 \( \mu \text{M} \), the blue color of oxidized TMB gradually fades out with a simultaneous decrease in absorbance at 653 nm and ultimately becomes colorless (Figure 15a). The reason for this visible change in color may be attributed to the second ongoing redox cycle where GSH is oxidized to glutathione disulphide with the simultaneous reduction of oxidized TMB (Scheme 2).

A good linear relationship is maintained between absorbance and concentration within the concentration range 0–80 \( \mu \text{M} \) with a correlation coefficient \( R^2 = 0.982 \) (Figure 15b). The limit of detection (LOD) is calculated to be 0.604 nM. The selectivity for the spectrophotometric detection of GSH is analyzed by adding Gly, Ala, Val, Pro, Cys, and GSH to the TMB–\( \text{H}_2\text{O}_2 \)–Au/OMC system under similar conditions. The \( \Delta \text{A} \) value at 653 nm is highest for GSH compared to others (Figure 16). This infers a good selectivity of the GSH assay with the developed sensor.

**CONCLUSIONS**

In summary, we have reported a hard template method for the synthesis of the Au/OMC catalyst from the AuNP-intercalated mesoporous silica (GMS) in one step without using any reducing agent. AuNPs of size approximately 10 nm are anchored on the surface of the porous carbon template of the catalyst without affecting the pore diameter of the OMC support. The Au/OMC catalyst proves to be a much more superior catalyst in comparison to bare mesoporous carbon CMK-3, SBA-15, and GMS for the electrochemical oxidation of methanol. The reduced Ohmic resistance at the electrode–electrolyte interface and resistance due to charge transfer, better stability of the material, small particle size, and highly porous surface area with a uniform distribution of AuNPs make Au/OMC an excellent catalyst in comparison to the three others for the MOR process. Besides, Au/OMC also exhibited a very good peroxidase-like activity and oxidizes TMB with a visible change in color at pH 4 which is monitored

![Figure 14. PL intensity study of the reaction between TPA and OH* radicals generated at 15 min interval where the concentration of TPA, \( \text{H}_2\text{O}_2 \), and Au/OMC are, respectively, 0.5 mM, 0.01 M, and 10 \( \mu \text{g} \).](image)
spectrophotometrically at 653 nm. Subsequently, we have also utilized Au/OMC successfully to detect GSH within a linear concentration range from 0 to 80 μM with a LOD of 0.604 nM.

## EXPERIMENTAL SECTION

### Materials

Pluronic P123, tetraethyl orthosilicate (TEOS), TESPTS, gold chloride trihydrate (HAuCl₄·3H₂O), sucrose, HF (40%), TMB, and H₂O₂ were purchased from Sigma-Aldrich. All other chemicals and solvents were purchased from a commercial source available locally and were used without further purification. The GMS precursor was synthesized by slightly modifying the method reported previously by Richards and co-workers.²⁶

### Synthesis of the Precursor Mesoporous GMS Template

Pluronic P123 (2.5 g) was dissolved in 94 mL of 2 M HCl in a round-bottomed flask at 318 K. Subsequently, a mixture of 5.57 mL of TEOS (25 mmol) and 0.5 mL TESPTS (1 mmol) was slowly added under stirring. Then, aqueous solution of HAuCl₄·3H₂O (0.4 g, 1 mmol) was added dropwise. The solution was stirred for 24 h at a temperature of 313 K and aged for 72 h at 373 K without stirring. The precipitated solid was filtered off and washed with water thrice followed by ethanol. The resulting solid was dried at 373 K for 24 h and calcined at 773 K for 5 h.

### Synthesis of Au/OMC

GMS (0.5 g) was impregnated with a solution of 0.625 g of sucrose in 2.5 g of H₂O and 0.07 g of H₂SO₄. The mixture has been kept in an oven and the temperature was maintained at 373 K for 6 h and then at 433 K for another 6 h. The black powder thus obtained was impregnated again with a solution of 0.175 g sucrose in 5 g of H₂O and 0.07 g of H₂SO₄ and kept in an oven similarly at 373 and 433 K. Finally, the solid obtained was carbonized in a tube furnace at 1173 K for 5 h under a nitrogen atmosphere. To remove the silica framework completely, the carbonized product was kept overnight in 10 wt % HF at room temperature and then centrifuged and washed with ethanol. Au/OMC obtained was dried overnight at 393 K in an oven.

### Physical Measurements

**Powder XRD.** Powder XRD was analyzed using a Philips PW 1140 parallel beam X-ray diffractometer with monochromatic Cu Kα radiation (λ = 1.540598 Å) operated at 40 kV and 40 mA using Cu Kα radiation (λ = 1.5418 Å) with a step size 0.008 and a scanning rate of 0.02 s⁻¹ in the 2θ range of 10°–100°. FESEM analysis was performed using a JEOL JSM 7610F instrument using an accelerating voltage of 15 kV. FESEM—EDS analysis and particle mapping were performed in the same SEM instrument equipped with an Oxford Instruments X-MaxN50 X-ray detector. TEM and TEM—EDS analysis, particle mapping, and scanning transmission electron microscope (STEM) dark field images of the catalyst were recorded using a JEOL 2100 TEM instrument operating at 200 kV. The elemental composition of the catalyst was determined by XPS measurements using a PHI 5000 Versa Prob II, FEI Inc. instrument. N₂ adsorption–desorption isotherms were performed using a NOVA 2200e surface area and pore size analyzer. The specific surface areas were calculated by the BET method, and the pore size distributions were calculated by the NLDFT method. The samples were degassed under a nitrogen flow at 373 K for 6 h to remove impurities adsorbed on the surface of the catalyst prior to the sorption experiment. A photoluminescent study was performed in a HORIBA Fluorolog spectrophuorimeter. UV–vis spectra and kinetic studies were performed in an Agilent 8453 diode array spectrophotometer.

### Electrochemical Studies

The electrochemical performances for electro-oxidation of methanol using the Au/OMC...
catalyst were studied by cyclic voltammetry at room temperature (25 °C) using a electrochemical analyzer CH Instrument CHI700E electrochemical workstation. A conventional three-electrode system was set up using glassy carbon (GC) as the working electrode, Ag/AgCl (saturated KCl) as the reference electrode, and Pt wire as the counter electrode. The GC electrode was cleansed thoroughly by 0.05 μm of alumina powder slurry followed by rinsing in distilled water and acetone and then dried in air. The Au/OMC sample solution prepared with 5 mg of catalyst in 10% Nafton solution was dropcasted on the GC electrode and then dried in air to use it as the working electrode. For a comparative study, the electro-oxidation of methanol was performed using the Au/OMC, as the working electrode. For a comparative study, the electro-dropcasted on the GC electrode and then dried in air to use it as the working electrode. For a comparative study, the electro-

Peroxidase-like Activity of Au/OMC. The peroxidase-like activity of the Au/OMC composite was investigated using TMB as the peroxidase substrate in acetate buffer solution in the presence of H2O2. For this, 2.4 μL of TMB (0.125 M stock solution) was dissolved in dimethyl sulfoxide) and treated with 4 μL of 30% H2O2 in the presence of 10 μg of the Au/OMC catalyst in acetate buffer (0.1 M, pH 4.0). The color change of the solutions was monitored spectrophotometrically in time-scan mode at 653 nm. The kinetic analysis with TMB as the substrate was performed with a fixed concentration of H2O2 (13 mM) and varying the concentration of TMB (4.16, 10.0, 20.0, 40.0, 60.0, 100.0, 125.0, and 156 μM) in the presence of 10 μg of Au/OMC catalyst. Similarly, the kinetic analysis with H2O2 as the substrate was performed using the same amount of catalyst with a fixed concentration of TMB (100 μM) and varying concentration of H2O2 (0, 13, 19.5, 26.1, 32.6, 39.1, 48.9, 58.7, 68.5, and 81.5 mM). Kinetic parameters were calculated based on Michaelis–Menten eq 6.

\[ V_0 = \frac{V_{\text{max}} [S]}{[S] + K_m} \]  

where \( V_0 \), \( V_{\text{max}} \), [S], and \( K_m \) represent the rate of conversion achieved by the reaction, maximum rate of conversion, the concentration of the substrates, and Michaelis–Menten constant, respectively.

Spectrophotometric Detection of GSH by Au/OMC Based on Its Peroxidase-like Activity. For the colorimetric assay of GSH, a series of solutions each with 13 mM H2O2, 10 μL of a 6.25 mM solution of TMB, 10 μg of Au/OMC catalyst, and 3 mL of acetate buffer were prepared at room temperature. The solutions were incubated at 40 °C for 10 min. To each solution, GSH is added at different strengths ranging from (0–300 μM) and change in absorbance at 653 nm was monitored spectrophotometrically.

Study of Photoluminescence with TPA. In order to prove the generation of the OH* radical, photoluminescence (PL) spectra were studied using TPA as a fluorescent probing agent. 0.5 mM TPA, 10 mM H2O2, 10 μg of Au/OMC catalyst were incubated in 20 mL of acetate buffer (pH 4.0) and stirred well. The PL spectra of the solutions were measured at an interval of 15 min after centrifugation and intensity of the emission peak produced at 439 nm (λem = 315 nm) due to OH* radical generation was monitored.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01880.

Resistive parameters obtained from electrochemical impedance spectroscopy, possible mechanistic pathways for methanol oxidation reaction in alkaline and acidic medium, oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB) by H2O2 in the presence of peroxidase enzyme, STEM images (dark field) of Au/OMC, SEM-EDX spectra of Au/OMC, SEM-EDX elemental mapping of Au/OMC at two different regions, cyclic voltammogram of Au/OMC in 1 M H2SO4 without methanol, current density comparison of Au/OMC, CMK-3, GMS, and SBA-15 in 1 M H2SO4 and 1 M NaOH saturated with N2 at a scan rate of 50 mV s⁻¹, electrochemical impedance spectroscopy of Au/OMC measured in comparison to CMK-3, colour of the solution containing TMB, H2O2, and AuOMC catalyst at different pH, and optimization of pH and temperature for the peroxidase-like activity of Au/OMC (PDF).

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Notes
The authors declare no competing financial interest.

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