Novel synthesis of crystalline mesoporous tin dioxide doped with nanogold

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Abstract

We report the successful synthesis of a new material, a crystalline mesoporous tin dioxide (m-SnO₂) framework that contains nanogold clusters (m-SnO₂-Au), prepared using a direct soft method under ambient pressure. The structure, bulk, and surface properties of this new material are analyzed and confirmed by N₂ adsorption–desorption analysis, powder X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), and UV-Vis spectroscopy. The material possesses a highBrunauer–Emmett–Teller (BET) surface area of 97 m²g⁻¹, a narrow pore size distribution (2.1 to 3.3 nm) with an average pore diameter of 2.7 nm, and an average pore volume of 0.06 cm³g⁻¹. We believe that the nanogold clusters initially occupy the pores of the mesoporous tin dioxide, thus restricting their growth before diffusing into the walls of tin dioxide during the second heat treatment. The median nanogold cluster size is 1.4 nm, indicating that this method controls both the porous structure and the size of the cluster within. The synthesized m-SnO₂-Au material has a relatively small bandgap of 3.0 eV, as determined using the Kubelka-Munk function. The UV-Vis and white-light optical sensitivities of m-SnO₂-Au are considerably higher than those of the parent material m-SnO₂.

Keywords: Doping; mesoporous tin dioxide; nanogold clusters; optoelectronic activity; soft templating synthesis.

1. Introduction

Tin dioxide is a semiconductor material with a wide bandgap of 3.6 eV (Aswaghosh et al., 2016; Popescu et al., 2001; Shaalan et al., 2016) that is employed in many applications; for example, in gas or vapor sensing (Wagner et al., 2011; Li et al., 2012; Tonegger & Hieu, 2012; Brunet et al., 2012; Chen et al., 2013) and in the determination of optical sensitivity (Huang et al., 2014; Yu et al., 2011; Ganose & Scanlon, 2016). It is known that the bandgap of a semiconductor can be tuned by doping it with other elements (Aswaghosh et al., 2016; Yu et al., 2011; Ganose & Scanlon, 2016; Morris et al., 2001; Manikandan et al., 2016), by creating more oxygen defects (Aswaghosh et al., 2016; Manikandan et al., 2016), or by changing the crystal size (Aswaghosh et al., 2016; Manikandan et al., 2016; Brus, 1984; Smith & Nie, 2011). On the other hand, producing mesoporous tin dioxide increases the surface area of the material from 30 m²g⁻¹, as a non-porous material (Benhebal et al., 2011), to about 100 m²g⁻¹ (Aqeel et al., 2016), depending on the heat treatment used. SnO₂ crystals increase in size as a result of heat treatment (Dieguez et al., 1996; Tunstall et al., 1999; Zhang & Liu 2000; Dieguez et al., 1996; Tunstall et al., 1999). This effect collapses the pores (the weakest part of the structure), thus decreasing the surface area at temperatures above 350 °C until the product eventually becomes flattened and nonporous (Severin et al., 1998). By creating a high surface area and decreasing the crystal size of the walls, the exposed contact surface area of the material increases, thereby leading to improvements in surface sensitivity, catalytic activity, and sorption ability. Nevertheless, introducing and maintaining the porosity of tin dioxide at multiple elevated temperatures has proved to be a challenging task (Aqeel et al., 2016).

A nanocluster size of 1 to 5 nm is important in order to induce quantum-effect properties and generate active surfaces (Gutierrez-Wing et al., 1997; Nancy-Xu et al., 2004). The surface plasmon behavior of nanogold clusters depends on various factors such as cluster size, the distances between clusters, and the substrate or matrix effect (Nancy-Xu et al., 2004; Okamoto & Yamaguchi, 2003). However, controlling the size of gold clusters without the use of inhibitors, such as micelles, surfactants, or organic compounds is rather difficult (Nancy-Xu et al., 2004; Gutierrez et al., 1999; Woehrle et al., 2002; Kumar et al., 2007). These inhibitors segregate the gold precursor, especially during wet chemistry processes, and minimize the aggregation of clusters when subjected to elevated heat treatment above 200 °C.

Previously, we reported a novel synthesis of mesoporous tin dioxide (m-SnO₂) that maintains its porosity and high surface area after being subjected to multiple heat treatments.
at temperatures of up to 500 °C (Aqeel et al., 2016). This feature enables post-cluster synthesis to be applied to the porous material, which requires further heat treatment. This procedure was employed in this work to produce m-SnO$_2$, with nanogold (Au) particles introduced by post synthesis. The post synthesis of Au was performed after ensuring that the pores had opened and were free or partially free of surfactant materials by extended Soxhlet extraction, followed by calcination to further remove remaining surfactants and strengthen the m-SnO$_2$ framework by condensation. Evacuation of the pores enhances diffusion of the Au precursor through the pores, while the pores segregate and limit the aggregation of Au particles during heat treatment. Such pores can be considered as nucleation sites that are utilized to restrict the growth of any guest clusters, in this case nanogold clusters, by the confinement effect. In addition, the inclusion of a reducing gas, such as H$_2$, is essential for the conversion of the Au precursor into its metallic form below room temperature; it also limits aggregation during heat treatment, since nanogold can sinter at temperatures as low as 330 °C, (Goudeli & Pratsinis, 2016). We found that this material is active in both the UV and the visible spectral region, and its optoelectronic activity increases significantly after the introduction of nanogold clusters into the m-SnO$_2$. The present findings suggest that m-SnO$_2$-Au may be employable as an optical catalyst for the photo-degradation of organic compounds such as phenol and its derivatives in water (Benhebal et al., 2013; Fatimah et al., 2015; Abdullah et al., 2016; Asiri et al., 2011; Aqeel & Bumajdad, 2017). It is known that phenol and its derivatives are toxic to both marine life and humans. These molecules are usually found in waste water that can be discharged or leaked into water resources (Ritson et al., 2014; Smith et al., 2015; Bakke et al., 2013). With this in mind, m-SnO$_2$-Au could be employed as an integral component of optoelectronic devices such as photovoltaic cells (Chen et al., 2013; Yu et al., 2011; Ganose & Scanlon, 2016; Fuchs et al., 2011), for the labeling of antigens and amino acids (Sawada et al., 2000; Loukanov & Gagov, 2012), to decrease heat transfer through glass by coating with SnO$_2$-Au (Chowdhury et al., 2005), and for harvesting of solar energy like plants using quantum-sized gold clusters (Magis et al., 2010). It is well known that the future of humanity rests on sustainable clean energy resources.

In this work, we demonstrate that the introduction of nanogold clusters into m-SnO$_2$ improves the electrical and optical properties of the final product in comparison to the parent m-SnO$_2$.

2. Experimental

2.1 Synthesis

2.1.1 Preparation of mesoporous SnO$_2$

Mesoporous SnO$_2$ was prepared by slowly stirring hexadecylamine (Alfa Aesar, analytical grade, 90%) (0.26 g) in PrOH (Alfa Aesar, 99%) (24.4 cm$^3$) until completely dissolved (colorless transparent solution was attained). Next, Sn(OPr)$_4$ (Alfa Aesar, 99%) (1.9 g) was added to the solution at room temperature such that the surfactant: solvent: Sn molar ratio was 0.2:60:1.0 (Aqeel et al., 2016). The reactants were stirred slowly under water-saturated air (approximately 80% humidity) at atmospheric pressure for 3 days. The obtained product was filtered and washed with deionized water and ethanol (Sigma Aldrich, 99.8%). The product was subsequently transferred to a Soxhlet extractor and extracted with ethanol overnight (approximately 16 h), in order to remove the surfactant, and was subsequently collected by filtration. The product was calcined at 300 °C for 2 h in air (heating rate of 2 °C min$^{-1}$). A portion of the synthesized m-SnO$_2$ (0.3 g) was dehydrated at 120 °C for 3 h under N$_2$ (grade 6, 99.9999%). NaAuCl$_4$ (Alfa Aesar, 99.99%) (0.005 g) was dissolved in methanol (4.5 cm$^3$) (HPLC grade 99.9%) at 0 °C and then mixed with the dehydrated-SnO$_2$ for 30 min under N$_2$. Subsequently, 2% H$_2$ in N$_2$ was introduced at room temperature until dryness. Finally the sample was heat-treated at 400 °C for 10 min under 2% H$_2$ in N$_2$, followed by cooling to room temperature under ambient air (heating rate of 3 °C min$^{-1}$). The H$_2$ gas was used to reduce the Au precursor by transforming it into metallic Au. The concentration of H$_2$ gas in N$_2$ is recommended to be under 5% to prevent explosions at elevated temperatures. All chemicals were used as received, without further purification.

2.2 Characterization

Powder X-ray diffraction (XRD) measurements were performed using a Bruker AXS D8 ADVANCE diffractometer with a copper target ($\lambda = 1.5418$ Å); the DIFFRAC$^+$ software was used for analysis, and the following operational parameters were employed: 40 kV; 40 mA; front slit window size 0.1 mm for low angle, 1.0 mm for wide angle scans; the deflection plate was placed at a distance of 0.5–1.0 mm above the sample for the low angle scan; continuous coupled two-theta scan/theta scan mode, 0.5 step/s. Nitrogen gas adsorption–desorption measurements were performed using a Micrometrics Tristar analyzer. High resolution transmission electron microscopy (HRTEM) imaging was performed using a JEOL JEM-2011 electron microscope operating at 200 kV. The images
were recorded using a Gatan 794 CCD camera. ImageJ software was used to analyze the TEM images. The TEM instrument was equipped with an Oxford Link ISIS Semi STEM energy dispersive X-ray diffraction (EDX) system, which was used for determining the chemical compositions of the samples. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo ESCALAB 250Xi spectrometer with a monochromator and an Al-Kα radiation source (1486.6 eV). The spectra were recorded and processed using an Avantage data system. The analyses were carried out using the following parameters: analysis chamber pressure of $10^{-9}$ Torr, step size of 0.1 eV, dwell time of 100 ms, and pass energy of 20 eV. All binding energy values were determined with respect to the C1s line (284.6 eV) originating from adventitious carbon. A flood gun was used in the standard charge compensation mode to neutralize the charge buildup on the surface of the insulating layer. Optical activation experiments were performed using an ENERGETIQ white laser-driven light source (LDLS). The distance was set to 7 cm (20–200 mW m$^{-2}$), and the UV source was an Hg tube lamp (24 W, 365 nm, 230 V, and 50–60 Hz) purchased from UniEquip. The current was measured at room temperature using an Agilent B2901A source/measure unit and two banana probes placed 4 mm apart. UV-Vis spectroscopy was performed using a Cary 5000 UV-Vis-NIR spectrophotometer (Version 1.12) with the following settings: abs mode 200–800 nm, scan rate 600.000 nm min$^{-1}$, data interval 1.000 nm, full slit height, double beam mode, signal to noise mode off, and baseline correction on.

3. Results and discussion
3.1. X-Ray diffraction

The low-angle XRD patterns of m-SnO$_2$ before and after the introduction of nanogold clusters (m-SnO$_2$-Au) are presented in Figure 1. The patterns clearly reveal that the main <100> diffraction peaks did not shift for both samples. Figure 1(a) shows the XRD pattern of mesoporous SnO$_2$ calcined at 300°C after the pores were evacuated of the templating material by Soxhlet extraction followed by calcination. Figure 1(b) shows that the mesoporous structure of m-SnO$_2$ remained intact after the synthesis of the nanogold clusters within its pores and the subsequent heat treatment, which was performed at 400 °C under H$_2$/N$_2$ to reduce the introduced gold precursor to metallic gold. The decrease in the intensity of the main diffraction peak associated with m-SnO$_2$-Au, relative to that of m-SnO$_2$ (Figure 1(b)), indicates that some pores were occupied by nanogold clusters; further evidence includes the observed decrease in the total surface area and pore volume, as detailed in the results of the N$_2$ sorption measurements, below. The d-spacing of the m-SnO$_2$-Au material was calculated from the low-angle XRD spectrum in Figure 1(b) and was found to be 68.0 Å. Furthermore, the distance between the centers of two adjacent pores ($a_0$) was found to be 78.5 Å. By subtracting the average pore size (27.0 Å), as determined from the N$_2$ sorption measurements (see Figure 3(d)), from this value, the average wall thickness was determined to be 51.5 Å; the HRTEM images in Figure 5(b) confirm that the SnO$_2$ crystal size was approximately 50 Å.

The wide-angle XRD patterns for m-SnO$_2$-Au and m-SnO$_2$, presented in Figure 2 confirm the crystalline nature of the samples; the structures of these materials were assigned to cassiterite SnO$_2$, in good agreement with JCPDS card 01-077-0447 (Aqeel et al., 2016). The peak intensities for m-SnO$_2$-Au (Figure 2(b)) were higher compared to those of m-SnO$_2$ (Figure 2(a)).
The difference in peak intensity can be attributed to the fact that the m-SnO$_2$-Au sample underwent two successive heat treatments, first at 300 °C, to strengthen the framework through further condensation and to remove any remaining organic templating material, and then at 400 °C to convert the Au precursor into nanometallic Au; whereas m-SnO$_2$ was calcined only once at 300 °C. Moreover, the broad diffraction peaks indicate that the m-SnO$_2$ crystals are small in size. By contrast, the nanogold clusters were too small, too few in number, and did not have regular repeating distances that could be detected by wide-angle XRD. Therefore, other methods such as XPS and EDX were used to detect and analyze the nanogold clusters.

3.2. $N_2$ adsorption–desorption measurements

$N_2$ sorption measurements were performed to determine the average pore sizes, average pore volumes, and total surface areas of the m-SnO$_2$-Au and m-SnO$_2$ materials. Figures 3(a) and 3(c) depict typical type-IV isotherms that are representative of mesoporous materials (Sing et al., 1985). Each isotherm can be divided into three main sections. The first section starts at the beginning of the isotherm, in the low-pressure region, and extends to the first point of inflection (just before a relative pressure of 0.2). This region corresponds to the start of monolayer to multilayer adsorption within the pore walls. The second section, which extends from the first inflection point to the second one (between relative pressures of 0.2 and 0.6) corresponds to capillary condensation within the pores and is indicative of the mean pore diameter.

The last section of the isotherm is a flat section ranging between relative pressures of 0.6 and 0.9, and represents multilayered adsorption on the external surface after complete filling of all pores. A small hysteresis loop is observed in Figure 3(c) for m-SnO$_2$-Au, lying between types H1 and H2 according to the IUPAC classification (Sing et al., 1985), and was observed during the desorption cycle between relative pressures of 0.55 and 0.4, indicating the existence of different pore shapes and sizes in this material. A type-H1 hysteresis loop is indicative of cylindrical pores whereas an H2 loop represents irregular pore shapes (Sing et al., 1985).

The pore size distributions of the synthesized materials, shown in Figures 3(b) and 3(d), are narrow, confirming that the proposed synthesis method provides excellent control over the pores size. The pore sizes of the m-SnO$_2$-Au sample were in the 21–33 Å range, with an average size of 27 Å; these pore sizes are consistent with mesoporous materials, as classified by IUPAC (Sing et al., 1985). The BET surface area of the synthesized m-SnO$_2$-Au material was 97 m$^2$/g, with a pore volume 0.06 cm$^3$/g, as presented in Table 1. This surface area is relatively high considering that the material has been subjected to two heat treatments and has nanogold clusters occupying some of its pores. These results indicate that this material has maintained its mesoporosity even after the synthesis of nanogold particles within its pores and subsequent heat treatments at 400 °C. By contrast, the $N_2$ sorption results for the mesoporous m-SnO$_2$ that was

![Fig. 3. $N_2$ adsorption–desorption isotherms for the mesoporous samples after the second heat treatment at 400 °C. a) m-SnO$_2$ and b) its pore-size distribution; c) m-SnO$_2$-Au and d) its pore-size distribution.](image-url)
subjected to a similar procedure, but without the insertion of the nanogold, displayed a BET surface area and pore volume of 113 m$^2$ g$^{-1}$, 0.07 cm$^3$ g$^{-1}$, respectively, and a maximum pore size of 23 Å (Table 1).

The isotherm produced by m-SnO$_2$ did not show any hysteresis, indicating a more uniform pore shape and smaller pore size distribution. The decrease in the BET surface area from 113 to 97 m$^2$ g$^{-1}$ might indicate that some of the nanogold clusters occupy the pores, which is in agreement with the decrease observed in the intensity of the main XRD peak, as shown in Figure 1(b).

3.3. X-ray photoelectron spectroscopy

The Sn and Au oxidation states in the sample, as well as the chemical linkages present, were investigated using XPS (Figure 4). The Sn peaks at 486.3 and 495.1 eV (Figure 4(a)) correspond to Sn$^{4+}$ 3d$_{5/2}$ and 3d$_{3/2}$ orbital splitting, which indicate the formation of the tin dioxide framework (Uddin et al., 2012; Zhao et al., 2012). The absence of an XPS peak at 493.6, resulting from 3d$_{3/2}$ orbital splitting caused by Sn–Au bonding, indicates that this type of bonding was not present. The oxygen XPS peak at 530.1 eV, which results from O1s orbital splitting, corresponds to O–Sn bonding in the SnO$_2$ framework. In addition, a smaller peak observed at 531.6 eV may indicate the existence of oxygen defects (vacancies) in the framework, and/or the presence of chemisorbed O$^-$ or OH$^-$ at the material surface/subsurface, in the form of tin-hydroxyl groups [Sn(OH)$_4$] (Uddin et al., 2012; Zhao et al., 2012) (see Figure 4(b)).

Table 1. Brunauer–Emmett–Teller (BET) surface areas, pore sizes, and pore volumes of m-SnO$_2$ and m-SnO$_2$-Au samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$g$^{-1}$)</th>
<th>Average pore size (Å)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-SnO$_2$ (calcined at 300 °C)</td>
<td>222</td>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>m-SnO$_2$ (calcined at 400 °C)</td>
<td>113</td>
<td>23</td>
<td>0.07</td>
</tr>
<tr>
<td>m-SnO$_2$-Au (calcined at 400 °C)</td>
<td>97</td>
<td>27</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Fig. 4. XPS spectra of m-SnO$_2$-Au.

The XPS peak at 83.4 eV corresponds to Au 4f$_{7/2}$ orbital splitting and indicates the existence of metallic gold (Rodriguez et al., 2014; Hostetler et al., 1998; Liu et al., 2013), whereas the XPS peak at 86.5 belongs to the Au 4f$_{7/2}$ of ionic gold (Liu et al., 2013) and is indicated by the arrow in Figure 4(c). We believe that ionic gold comes from unreduced gold chloride precursor that has escaped the reducing heat treatment. The percentage weight of chloride (wt %) determined from the XPS 2p orbital at 197.9 eV is 0.7 wt%. This Cl ion is believed to be associated with the ionic Au in the NaAuCl$_4$ precursor; when divided by 3, this amount becomes 0.2 wt% when compared to the total amount of Au (3.5 wt % detected by EDX), and is thus equal to only 5% of the total gold present in the sample.

3.4. High-resolution transmission electron microscopy

HRTEM analysis was performed on the m-SnO$_2$-Au sample. Figure 5(b) shows an HRTEM image recorded from the edge of the particle whose TEM image is shown in Figure 5(a); the crystal diffraction planes reveal that the lattice fringes match those of SnO$_2$ and the crystal sizes are within 5 nm. These crystal sizes are very similar to those calculated from the XRD pattern given in Figure 1 using the Scherrer equation.
Figure 5(d) shows the dark-field TEM image corresponding to that shown in Figure 5(c) and provides further detail about the overall distribution of nanogold clusters in the matrix (the bright spots). In addition, the image in Figure 5(f) clearly shows that the porosity of the structure is spread through the entire sample. Moreover, the pore sizes were determined to be in the range of 2.4 to 5 nm, with nanogold cluster sizes of 0.7–2.1 nm (measured using the ImageJ software). The Au clusters locations are inside and close to the pores, clearly indicating that they have diffused into the m-SnO$_2$ framework, as evidenced by the dark round spots at the left edges of Figure 5(f), inside the red rectangle and marked by the red lines and circles on the enlarged image, as well as in Figures 5(a) and 5(c). We suspect that diffusion has occurred during the heat treatment under the H$_2$/N$_2$ reducing gas at 400 °C. At this temperature, under reducing conditions, the gold precursor tends to form metallic nanogold clusters. However, the sizes of the clusters are restricted by the pore walls. It is thought that if the gold precursor existed initially outside of the pores, it would have aggregated to form larger clusters, such as the one indicated by the red circle in Figure 5(e); this cluster is around 55 nm in size. These results highlight the important role of porosity in restricting the size and growth of nanoclusters.

3.5. Energy dispersive X-ray diffraction
EDX measurements were performed on the sample to confirm its surface and near-surface compositions; two representative spectra are shown in Figure 5, clearly revealing the K-lines of O, and the L-lines of the Au and Sn atoms that exist in the material. The Cu K- and L-lines belong to the specimen grid. The total percentage weight of Au determined by EDX is 3.5%.

3.6. UV-Vis spectroscopy and optical sensitivity
3.6.1. UV-Vis diffuse reflectance transmission technique
The UV-Vis diffuse reflectance transmission (DRT) technique was employed to study both m-SnO$_2$ and m-SnO$_2$-Au samples and the corresponding spectra are presented in Figure 6(a). The m-SnO$_2$-Au sample exhibited a higher transmission than the m-SnO$_2$ sample. A Tauc plot was constructed using the data obtained by DRT to determine the bandgaps of these materials, employing the Kubelka-Munk function (F(K-M)(R)) as shown in the equation: F(K-M) = (1-R)$^2$/2R, where R is the percentage of reflectance transition. A graph was constructed to directly determine the bandgaps by plotting [F(R) x E$^2$] against the photon energy (E) in electron volts (eV).

Fig. 6. (a) UV-Vis diffuse transmission reflection spectra, and (b) Tauc plots of the Kubelka-Munk function versus photon energy for the m-SnO$_2$ sample, and the m-SnO$_2$-Au sample, both calcined at 400 °C.

The bandgap ($E_g$) was determined by extrapolating the linear part of the curve to the intersection with the energy axis, as shown in Figure 6(b). The band gaps for m-SnO$_2$ and m-SnO$_2$-Au were determined to be 3.3 eV and 3.0 eV, respectively; both are considerably lower than the macrostructure value of 3.6 eV. A smaller bandgap could indicate the existence of oxygen defect sites, which form a new intermediate
density-of-state band that facilitates charge transfer at the metal–semiconductor interface (Manikandan et al., 2016). The contribution of nanogold plasmonic electrons that were excited by UV irradiation would have increased the electron density of the entire matrix (Chen et al., 2013; Huang et al., 2014; Ganose & Scanlon, 2016; Nancy-Xu et al., 2004; Okamoto & Yamaguchi, 2003).

3.6.2 Optical sensitivity
3.6.2.1. UV experiments
In these experiments, the samples were exposed to 320-nm UV light for 300 s, after which the UV source was extinguished and the sample was monitored for further 400 s; currents were measured over the entire 700 s of these experiments (Figure 7). For each sample, the current was observed to increase during the exposure to UV light, and then decrease once the UV source was extinguished. This behavior may indicate that the valance electrons were sufficiently excited to hop from the valance band to the conduction band as a result of the absorption of UV-light energy, thus crossing the bandgap barrier. The energy produced by the UV lamp was 3.8 eV, whereas the bandgaps measured for m-SnO₂ and m-SnO₂-Au samples were 3.3 and 3.0 eV, respectively. Moreover, the maximum current produced by m-SnO₂-Au was 850 μA (Figure 7), that is, more than 386 times higher than that produced by m-SnO₂ (2.2 μA) under the same experimental conditions. These results confirm that the bandgap of the m-SnO₂-Au sample is smaller than that of m-SnO₂ and that additional electrons may be produced by the nanogold (plasmonic effect) to increase the conductivity of the sample. This experiment verifies that both materials can be activated by UV energy.

3.6.2.2. Visible white-light experiments
The optical sensitivity (optoelectronic activity) of the samples under visible white-light conditions was also investigated. The current produced by the samples during exposure to white light is shown in Figure 8. The m-SnO₂-Au sample produced a maximum current of 112 μA (Figure 8(a)), which is 70 times higher than that produced by the m-SnO₂ sample (1.6 μA, Figure 8(b)) under the same experimental conditions. This result confirms that these materials can also be excited by visible light and may be employable in

![Fig. 7. Excitation of samples by UV light and the corresponding current measured on the surface of each sample: a) m-SnO₂-Au and b) m-SnO₂.](image)

![Fig. 8. Excitation of the samples by visible light and the corresponding current produced on the surface of each sample: (a) m-SnO₂-Au and (b) m-SnO₂.](image)

4. Conclusions
A new crystalline mesoporous tin dioxide framework containing nanogold clusters (m-SnO₂-Au) was successfully synthesized. This new material has a BET surface area of 97 m²g⁻¹, a mean pore size of 2.7 nm, and a pore volume 0.06 cm³g⁻¹. Initially, following the post-treatment of porous SnO₂, the nanogold clusters occupied the pores of the mesoporous tin dioxide framework, which restricted their further growth. Some of these clusters subsequently diffused into the walls of the tin dioxide as a result of the heat treatment, as evidenced
by HRTEM. The average nanogold cluster was 1.4 nm in size. The m-SnO$_2$-Au sample exhibited a bandgap of 3.0 eV, which is narrower than that of m-SnO$_2$, as determined using the Kubelka-Munk function. The new material described is optically excited by both UV and visible light, and may find utility in both optical and electronic applications.

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طريقه مبتكره في صناعه ثاني أكسيد القصدير البلوري والميزومسامي يحتوي على حبيبات ذهب نانومترية

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الملخص

لقد قمنا بصناعه ثاني أكسيد القصدير البلوري الميرو مسامي المرصع بحبيبات الذهب النانومترية بطريقة مبتكرة باستخدام الطريقه المباشره للقوارب الطرية تحت الضغط الجوي السائد. كما قمنا بتشخيص والتعرف على مكونات السطحية والتركيب الأساسي وخلاص هذه المادة الجديدة باستخدام الفحوصات التالية: فحص المسامه برذر أميت/ائر وفحص أشعه أكس المتشتته والحيود الفلوروسنطية والمكبر الإلكتروني عالي الدقه والأشعة المرئيه الفوق بنفسجية.

وقد أثبتت هذه الفحوصات أن المادة الجديدة تحتوي على مساحه سطحية عاليه 97 متر لكل جرام وتغلغلت إلى حوائط ثاني أكسيد القصدير أثناء تعرضها للمعالجه الحرارية الثانية. وكان متوسط قياس حبيبات الذهب يقارب 1 نانومتر وهذا يبين أن هذه الطريقه المبتكرة يمكننا السيطره على قياس الحبيبات المتكونه وايضا قياس المسام بالماده الأم. وأيضا قمنا بتحديد وقياس الفجوه الحزيمه لهذه المادة بطريقة كيبورك- منك وهي تساوي 3 اللكترون فولت. وأيضا قمنا بقياس الحساسه الضوئيه لهذه المادة الجديدة مقارنا بالماده الأم (ثاني اكسيد القصدير الميرو مسامي) فوجدنا أن المادتين لها نشاط كهروضوئي تحت تأثير الضوء المرئي والأشعة فوق بنفسجية ويتأثران أكثر بالأشعة الفوق بنفسجية كما تبين أن نشاط الكهروضوئي للماده الجديدة يفوق نشاط الماده الأصليه بثلاث المرات.