Comparison of functionalized and unfunctionalized mesoporous TiO_2 films as an efficient substrates for loading gold clusters; photocatalytic water splitting reaction investigation

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1. Problems and solutions

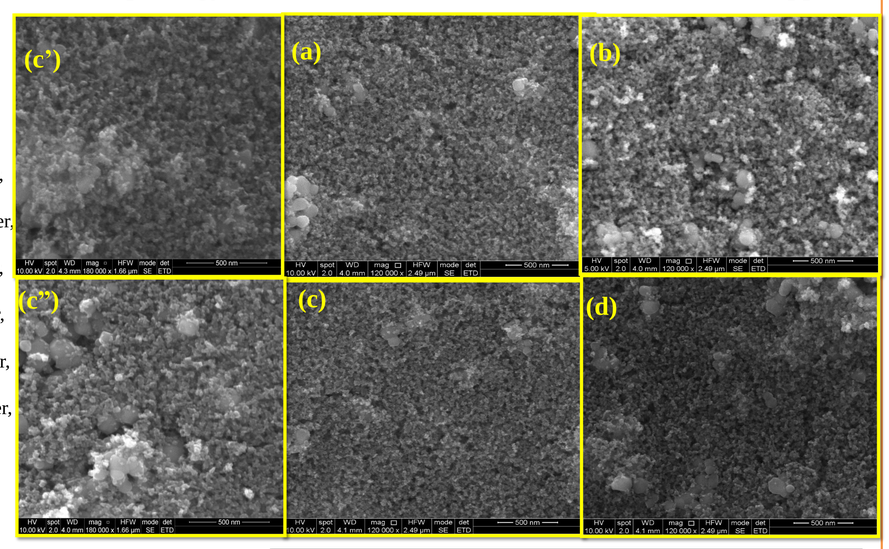
- Hydrogen possesses significant potential as an alternate fuel. Several technologies can be used to generate hydrogen. However, only a few of them can be considered as truly environmentally friendly.
- Regarding the free energy available in sunlight and the water abundance, the conversion of water to H_2, water splitting reaction, by using solar energy is promising, clean, low cost and eco friendly procedure.
- The semiconductors normally used as photocatalysts are bad catalyst for hydrogen evolution reaction (HER). Therefore the semiconductor particles are often loaded with noble metals to improve the surface reaction kinetics. If the size of noble metals is reduced, it leads to a remarkable improvement in the catalytic activity.
- Gold nanoclusters (Au NCs) are smaller in size than Au nanoparticles with diameters less than or equal to 2 nm and are suitable to modify surface properties.
- Agglomeration of NCs leads to an increase in NC size, eventually forming NPs, and should be avoided otherwise the agglomeration strongly affects the photocatalytic properties of the catalyst.
- Application of mesoporous TiO_2 semiconductor with remarkable surface defects, high surface area, and extensive 3D pore network can be beneficial to prevent agglomeration of gold clusters.
- Functionalization of the surface can be used to have stronger interaction between Au NCs and semiconductor surface leading to decrease the agglomeration and to increase the loading of the Au NCs to have a system with highly active sites and high number of active sites, respectively.

2. Photocatalyst Preparation

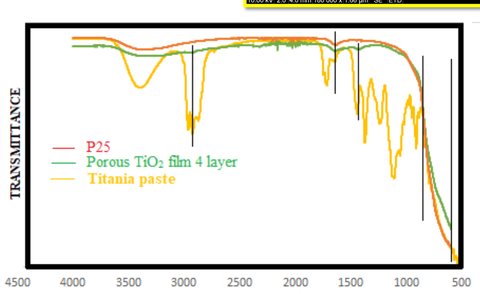
Making samples via this method can be divided into three steps: 1-Target production is by screen printing method. 2-Functionalization by grafting the prepared $MTiO_2$ surface to some chemicals contains of NH such as aminopropyltrimethoxysilane (APTMS). 3-Deposition of prepared gold clusters onto the surface (see the graphical abstract).

2. Photocatalyst Preparation

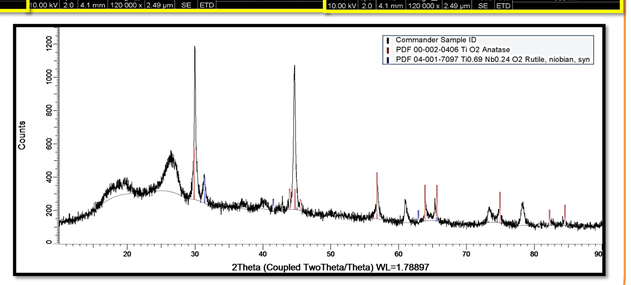
This work focuses on the establishment of the easy method to synthesize functionalized and unfunctionalized mesoporous titania films decorated gold nanoclusters and the investigation of their photocatalytic activities in water-splitting reaction. For determining the porosity size of different kinds of prepared films, we used **FESEM** and as seen in the fig. the average size is around 4-10 nm and porosity size between 2-50 nm is consistent with mesoporous material. Even after functionalization (c"), there are not many changes in porosity size and surface morphology, and it conforms that functionalization has happened in thin layer.



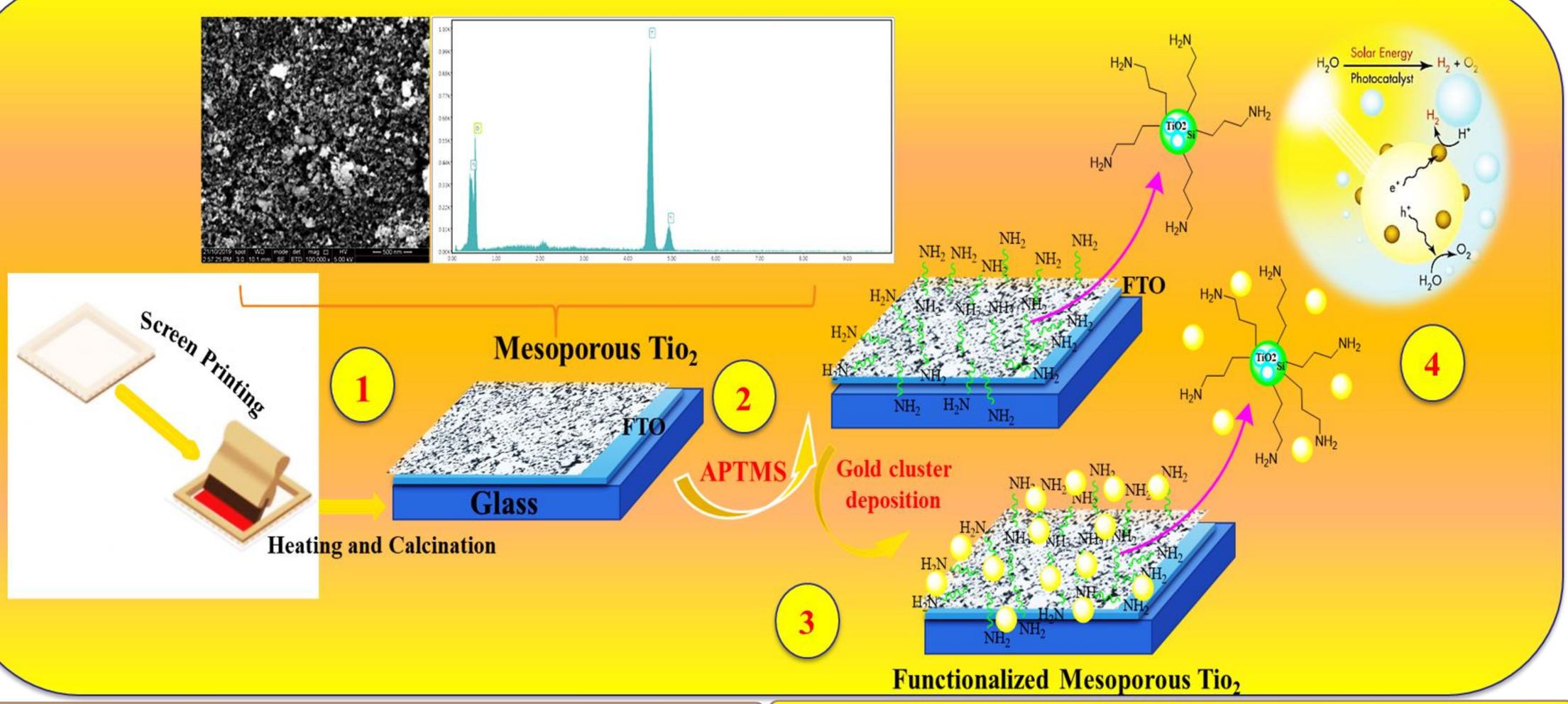
(a) ProusTiO_2 film with 4 layer, 500 nm-500/30min
(b) PorousTiO_2 film with 2 layer, 500 nm-500/30min
(c) ProusTiO_2 film with 4 layer, 500 nm-500/2:30 hr.
(d) ProusTiO_2 film with 4 layer, 500 nm-600/30 min.
(c') ProusTiO_2 film with 4 layer, 500 nm-500/2:30 hr./Au
(c") ProusTiO_2 film with 4 layer, 500 nm-500/2:30 hr./APTMS



FTIR of 4-layer TiO_2 film



XRD analysis of 4-layer TiO_2 film on FTO



3. Research Aims

- Increasing the number of active sites
- Reusability of the photocatalyst
- Investigation of activity of the prepared photocatalysts in water splitting reaction.

4. Characterization methods

1-SEM: Morphology of the surface and porosity size,
2-EDS: Elemental composition
3-FTIR: Information about chemical bonding, and molecular structure
4-XPS: Elemental composition
5-XRD:Identifying the type of crystalline phases
6-TGA: Approving template removal

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