Supplementary Information

Aminosilicate Sol-Gel Supported N-Doped TiO_2–Au Nanocomposite Materials and their Potential Environmental Remediation Applications

Alagarsamy Pandikumar[a], Kumarsrinivasan Sivaranjani[b], Chinnakonda S. Gopinath[b] and Ramasamy Ramaraj[a,*]

[a]*Centre for Photoelectrochemistry, School of Chemistry
Madurai Kamaraj University, Madurai-625 021, India
[b]Catalysis Division, National Chemical Laboratory, Pune-411 008, India

Experimental Details

Characterization techniques

The synthesized APS/$(N\text{-}P25\text{-}Au)_{NCM}$ were characterized by various techniques. The UV–visible diffuse reflectance spectra of the samples were recorded using a Shimadzu UV-2550 UV–vis spectrophotometer fitted with ISR-2200 DRS accessory. Photoluminescence spectra were recorded using a JASCO-FP-6500 spectrofluorimeter. HRTEM images were recorded using JEOL 3010 transmission electron microscopy with operating voltage at 300 kV. X–ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance with Cu Kα radiation (λ = 1.54178 Å). The chemical nature of Au and N in TiO_2 was studied using X-ray photoelectron spectroscopy (XPS) in a VG Microtech Multilab ESCA 3000 spectrometer with non-monochromatized Al KR X-ray (hν = 1486.6 eV). Raman spectra were recorded in a LabRAM High Resolution 800 UV Confocal Raman microscope with green laser (He-Ne 532.14 nm).

Brunauer–Emmett–Teller (BET) surface area analysis was carried out using Micrometrics Gemini 2375 surface area analyzer.

Carbon monoxide (CO) oxidation studies

The catalytic oxidation of carbon monoxide (CO) oxidation was carried out using a fixed bed reactor (14 mm diameter) under atmospheric pressure and the details of reactor setup can be found elsewhere.[1,2] Brooks mass flow controllers were used to control the gas flow of N_2, O_2 and CO. The reactor was placed in a tubular furnace with a uniform heating zone of 4 cm and temperature of the furnace was controlled using Radix 6400 temperature controller. A K-type thermocouple placed in a thermowell over the catalyst was used to measure the catalyst bed temperature. A reaction gas containing 5 % CO was passed over 250 mg of catalyst. The hydrogen reduction pretreatment on the catalyst was carried out at elevated temperature. The flow rate of the reaction gas mixture was 25 mL/min ($CO:O_2:N_2$ = 1:5:19) and the calculated gas hourly space velocity (GHSV) was 6000 cm^3/gm/h. The conversion reported here was the steady state data where catalyst was ramped at 2 °C and held at different temperatures for 10 min for equilibration. The reported data were collected at 5 min interval and was found to be consistent. The reactor outflow was analyzed using a gas chromatograph equipped with online gas sampling valve, 91.44 cm molecular sieve 13X column and thermal conductivity detector (TCD). All the catalytic test runs were carried out from room temperature to 300 °C.

Photocatalytic studies

The photocatalyst film was prepared by dispersing 250 mg of APS/$(N\text{-}P25\text{-}Au)_{NCM}$ in 5 mL ethanol and then sonicated for 5 min to ensure the homogeneous dispersion. The colloidal solution was coated as a film on a glass plate (1 cm^2) by casting a known volume of the solution

and then allowed to dry in air at room temperature. Then the film was annealed at 450 °C for 30 min. The P25, N-P25 and APS/$(P25\text{-}Au)_{NCM}$ films were also fabricated using the same procedure. The APS/$(N\text{-}P25\text{-}Au)_{NCM}$ film coated on a glass plate was immersed into a photolysis cell containing a mixture of 1 mM $HgCl_2$ and 10 mM oxalic acid (OA) and then irradiated with light source. Before illumination, nitrogen was purged into the reaction mixture for 30 min in dark. The reaction mixture was stirred at a constant speed during illumination. A 450 W Xenon lamp was used as the light source with a water filter cell (6 cm path length with pyrex glass windows) to cut-off IR and UV-B radiations. This water filter cell transmitted light from ~340 nm onwards. The distance between the light source and the photocatalyst coated glass plate was 60 cm. The sample aliquots were taken from the reaction sample at regular time intervals and were tested for their concentration. The Hg(II) ions concentrations were estimated by Dithizone method by analyzing the complex formed upon the addition of colorimetric reagent 1,5-diphenylthiocarbazone.[3]

References

1 A. C. Sunil Sekhar, K. Sivaranjani, C. S. Gopinath, C. P. Vinod, *Catal. Today,* 2012, **198** 92.

2 T. Mathew, N. R. Shiju, V. V. Bokade, B. S. Rao, C. S. Gopinath, *Catal. Lett.*, 2004, **94**, 223.

3 H. Khan, M. J. Ahmed, M. I. A. Bhanger, *Anal Sci.***,** 2005, **21**, 507.

Figures and Caption

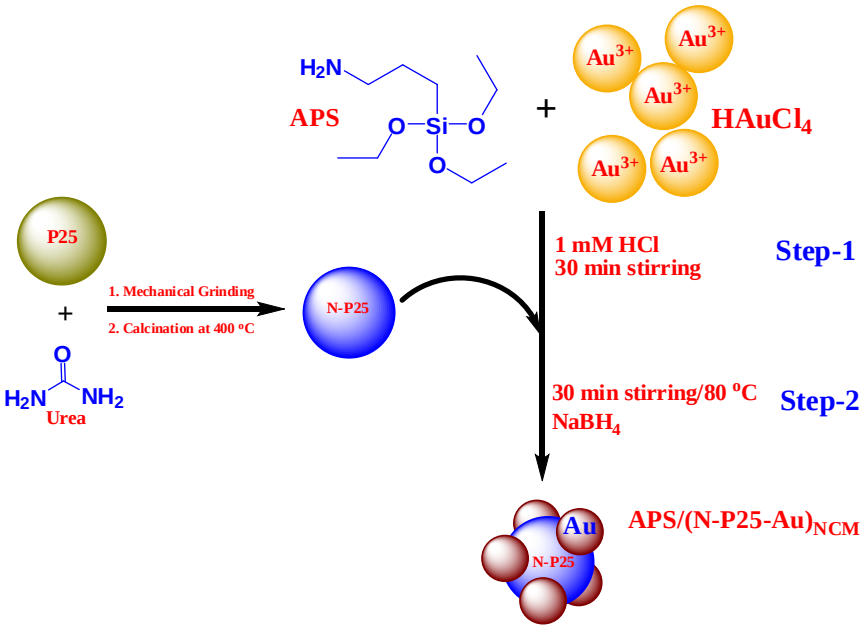

Fig. S1. Schematic representation of synthesis of APS/(N-P25-Au)$_{NCM}$ nanocomposite materials.

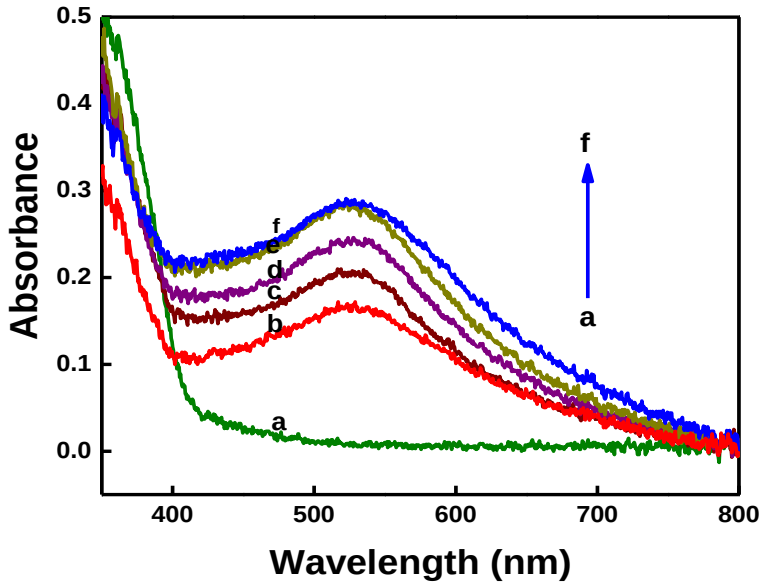

Fig. S2. Absorption spectra of (a) N-P25, (b) APS/(P25-Au)$_{NCM}$ (1 Wt.% Au), (c) APS/(N-P25-Au)$_{NCM}$ (1 Wt. % Au), (d) APS/(N-P25-Au)$_{NCM}$ (2 Wt.% Au), (e) APS/(N-P25-Au)$_{NCM}$ (3 Wt.% Au) and (f) APS/(N-P25-Au)$_{NCM}$ (4 Wt. % Au) nanocomposite materials.

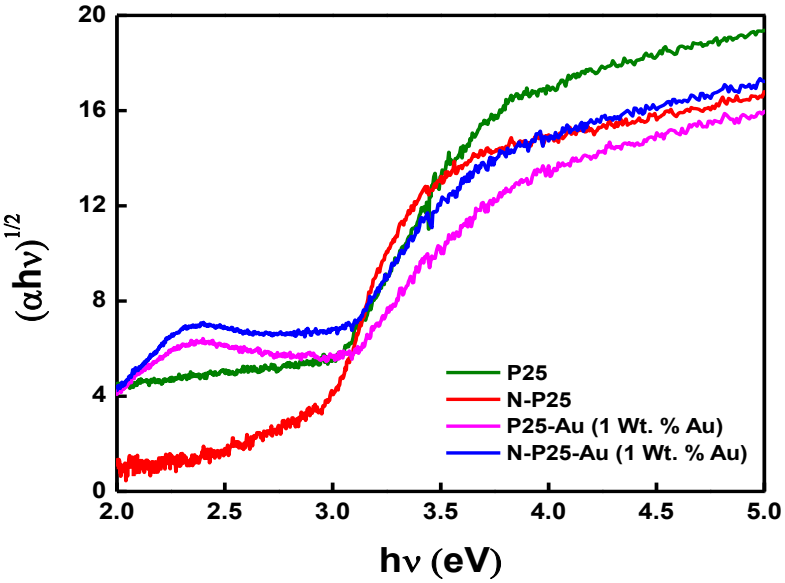

Fig. S3. Plots of $(\alpha hv)^{1/2}$ versus *hv* obtained for (a) P25, (b) N-P25, (c) APS/$(P25\text{-}Au)_{NCM}$ (1 Wt.% Au) and (d) APS/$(N\text{-}P25\text{-}Au)_{NCM}$ (1 Wt.% Au) nanomaterials.

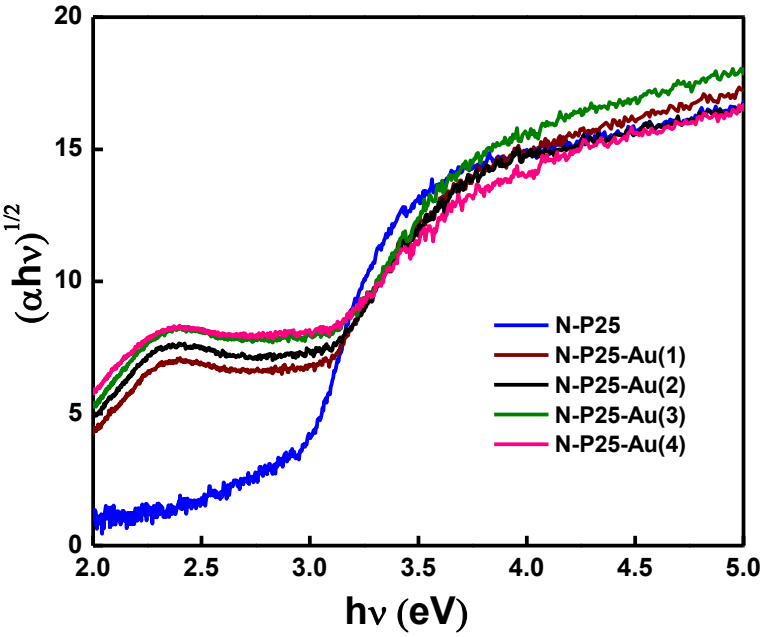

Fig. S4. Plots of $(\alpha hv)^{1/2}$ versus *hv* for obtained (a) N-P25, (b) APS/$(P25\text{-}Au)_{NCM}$ (1 Wt.% Au), (c) APS/$(N\text{-}P25\text{-}Au)_{NCM}$ (2 Wt.% Au), (d) APS/$(N\text{-}P25\text{-}Au)_{NCM}$ (3 Wt.% Au) and (e) APS/$(N\text{-}P25\text{-}Au)_{NCM}$ (4 Wt. % Au).

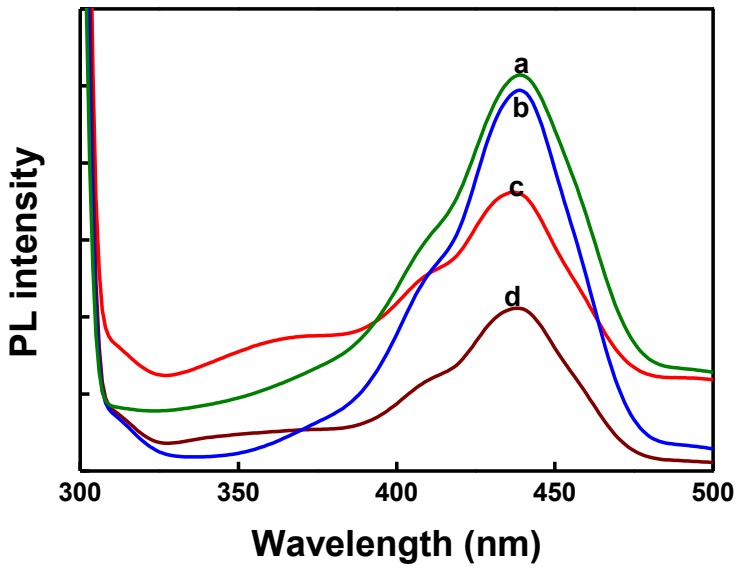

Fig. S5. Photoluminescence spectra of (a) P25, (b) N-P25, (c) APS/(P25-Au)$_{NCM}$ (1 Wt.% Au) and (d) APS/(N-P25-Au)$_{NCM}$ (1 Wt.% Au) nanomaterials in ethanol at λ_{ex} of 280 nm.

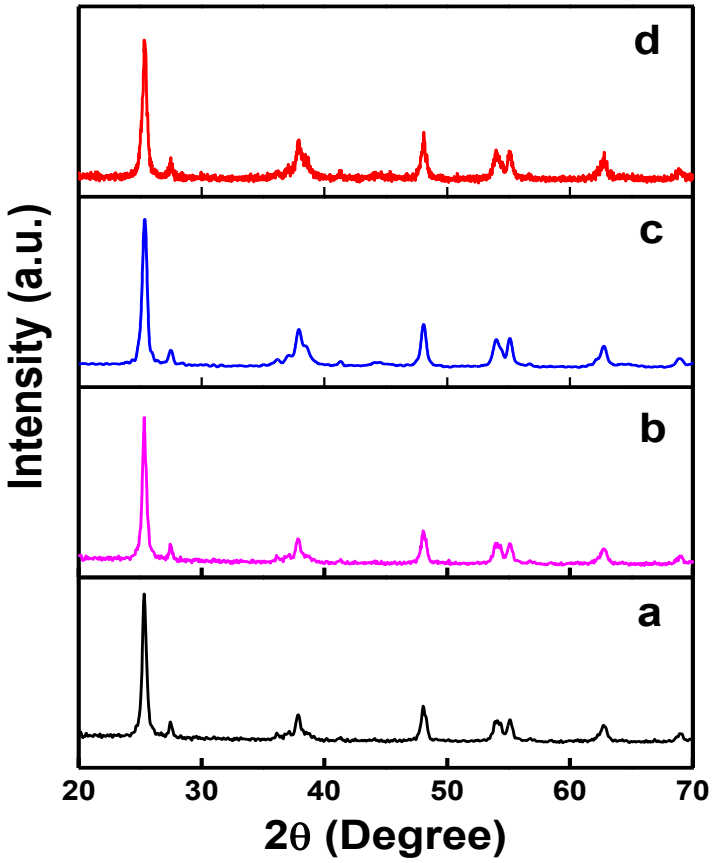

Fig. S6. XRD patterns of (a) P25, (b) N-P25, (c) APS/(P25-Au)$_{NCM}$ (1 Wt.% Au) and (d) APS/(N-P25-Au)$_{NCM}$ (1 Wt.% Au) nanomaterials.

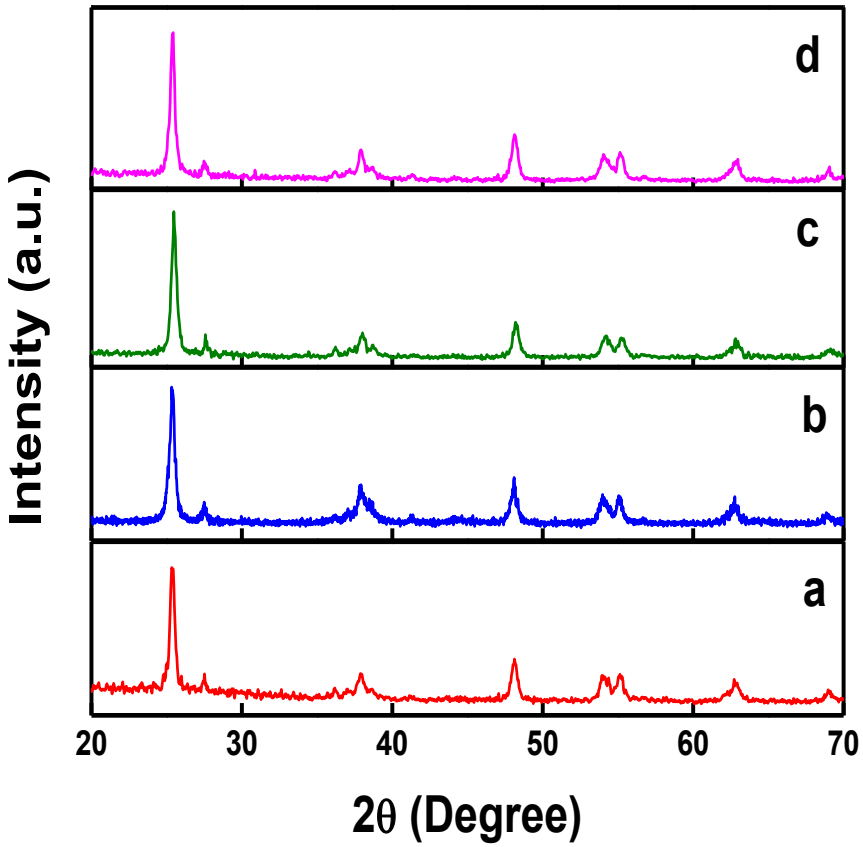

Fig. S7. XRD patterns of APS/(N-P25-Au)$_{NCM}$ with (a) 1, (b) 2, (c) 3 and (d) 4 Wt. % Au content.

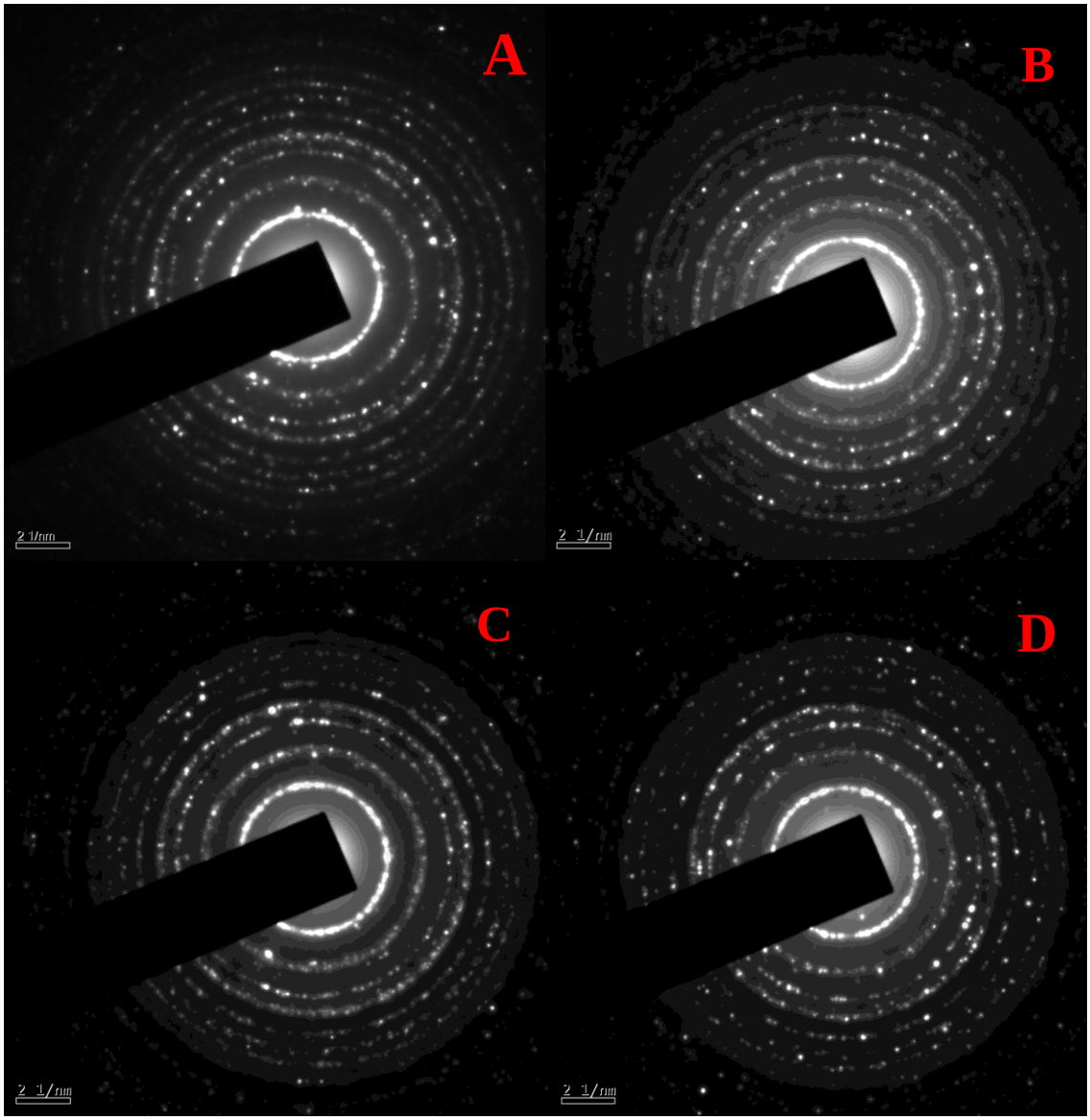

Fig. S8. SAED patterns of (A) P25, (B) N-P25, (C) APS/(P25-Au)$_{NCM}$ (1 Wt.% Au) and (D) APS/(N-P25-Au)$_{NCM}$ (1 Wt.% Au) nanomaterials.

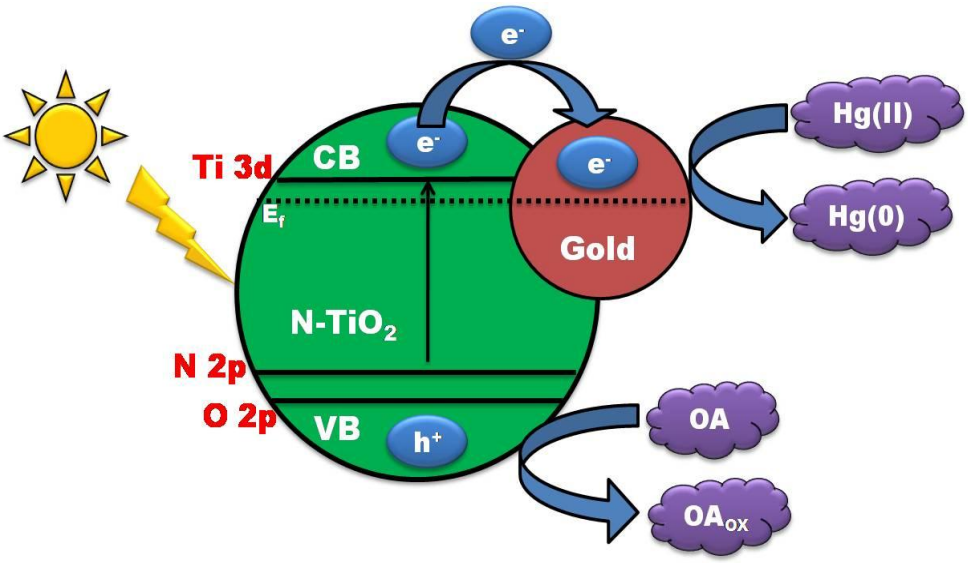

Fig. S9. Schematic representation of photocatalytic reduction of Hg(II) ions at the APS/(N-P25-Au)$_{NCM}$ film photocatalyst.