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Enhanced Photocatalytic and electrochemical properties of Au nanoparticles supported TiO_2 Microspheres

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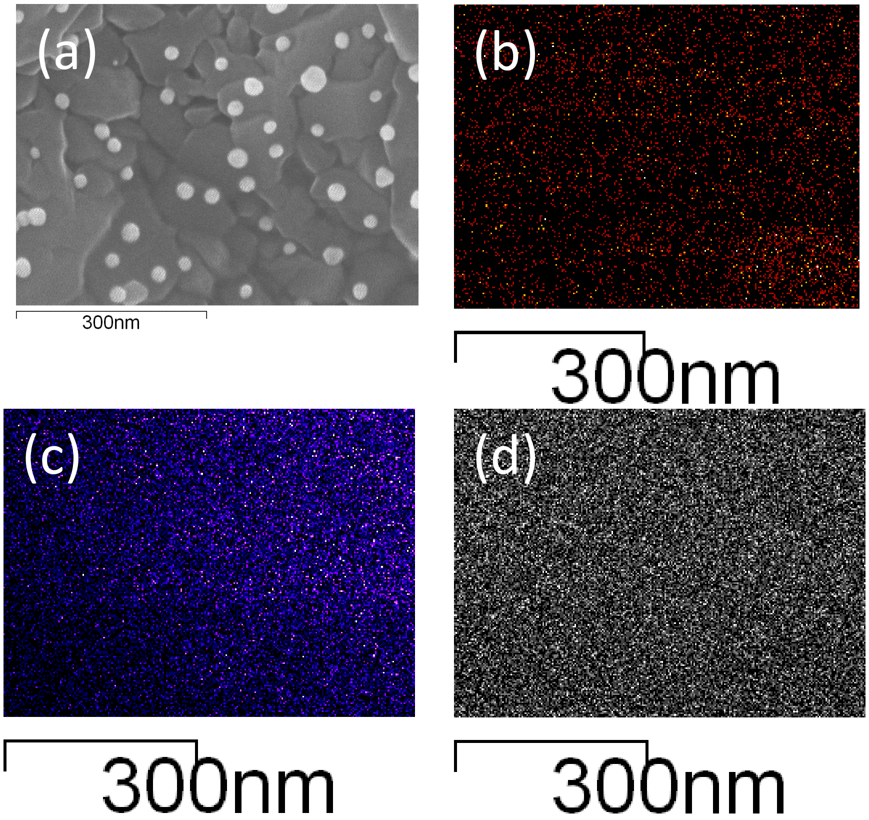

Fig. S1 Bright field SEM image of the (a) Au/TiO_2 composite; elemental mapping images of (b) Au (c) O and (d) Ti.

Functional Mechanism of Enhancement of Photocatalytic Activity of TiO_2 by Au NPs.

As the photocatalytic reaction is strongly influenced by the metal and surface structure of the material. Therefore, one of the main aims behind the modification of TiO_2 with Au NPs is to improve or tune its catalytic and sensing properties. The deposition of Au NPs on TiO_2 microspheres is an effective way for improving the photocatalytic efficiency as the Au NPs modifier can indirectly influence the interfacial charge transfer processes.

In photocatalytic process, the photocatalytic degradation of the organic compounds depends upon the availability of the carriers (electrons (e^-) and holes (h^+)) and their recombinitation rate. The slower the recombination rate of the charged carriers, the faster is the degradation of the organic dye. Generally in photocatalytic oxiditation oprocess, light of certain energy equal or greater the band gap of the semiconductor material excites the electrons from its valance band to the conduction band leaving behind the same number of holes on the valance band. These excited electrons are trapped by the absorbed oxygen (O_2) to form super oxide radical ions ($\bullet O_2^-$) which further react to form hydroxyl radicals (•OH) which are high are highly reactive to oxidize the organic material. Simultaneously the holes (h^+) at the valance band can easily react with the surface hydroxyls (OH) to produce hydroxyl radicals (•OH). The •OH species are highly reactive to oxidize the organic contaminants. However, the photogenerated electrons (e^-) and hole (h^+) may also recombine to reduce the available photocatalytic efficiency. This recombinitation of the carrier may be avoided/prevented by removing/transferring the conduction band electrons to somewhere else in the system to continue the mechanism. This is achieved by attaching some noble metals on the semiconductor surface which acts sink for photo generated electrons by suppressing the electron—hole pair (e^-—h^+) recombination and eventually oxidizing the contaminants by OH radicals.

Therefore Au nanoparticles were imbedded on the TiO_2 microspheres. In this way a metal—semiconductor junction is formed and barrier developed on the metal—semiconductor interface. As the work function of Au is higher than that of the semiconductor its Fermi energy level lies higher than that of TiO_2 microspheres. Therefore, before UV irradiation the electrons will flow from TiO_2 towards Au in order to equilibrate the Fermi level. Now the Fermi level of metal—

semiconductor is equal but the semiconductor (TiO_2) band is higher than that of the matal (Au). Therefore when Au/TiO_2 microspheres are irradiated by UV light, the electrons will flow from TiO_2 to Au leaving behind the same number of h^+ at the TiO_2 surface. The holes resides on the TiO_2 surface due to the barrier developed on the metal—semiconductor interface therefore Au acts as electron sink by reducing the e^-—h^+ recombination and prolonging the life time of e^-—h^+ pair. Eventually the e^-s on the Au surface are discharged to the solution and hence trapped by the absorbed oxygen (O_2) to form super oxides radicals (•O_2^-) which further form hydroxyl radicals (•OH). Simultaneously the h^+s at the semiconductor surface are captured by surface hydroxyls to generate hydroxyl radicals (•OH). These •OH species oxidize the organic contaminants due to their high oxidative efficiency.