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Photodeposition of AuNPs on metal oxides: Study of SPR effect and photocatalytic activity

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ABSTRACT

Effect of photodeposition of AuNPs (gold nanoparticles) on TiO_2, CeO_2, Cu_2O and Fe_3O_4 supports has been illustrated on sacrificial donor based hydrogen evolution. The synthesized samples were characterized by diffuse reflectance spectroscopy (DRS), and transmission electron microscopy (TEM). Highest photocatalytic activity was exhibited by Au/TiO_2 followed by Au/Fe_3O_4, Au/CeO_2 and Au/Cu_2O. Au/TiO_2 under optimized conditions has shown significantly high photocatalytic activity under both UV–visible and visible radiation. Au/TiO_2 shows hydrogen evolution rate of 920 μmol h^{-1} and 32.4 μmol h^{-1} under UV–visible and visible radiation, respectively. Significant enhancement in hydrogen evolution rate under visible light is very encouraging and may be attributed to polydispersed nature of AuNPs wherein larger particles facilitate light absorption and the smaller function as catalytic sites. Further studies are in progress to study the influence of various parameters on photocatalytic activity of Au/TiO_2.

1. Introduction

In pursuit of finding an alternative source of renewable energy, the current research scenario is primarily focussed on photocatalytic solar hydrogen production as it promises a clean and green route of generating hydrogen. Over the years, TiO_2 has garnered a lot of attention in the field of photocatalysis, courtesy its abundance, non-toxicity and low cost. However, the major hurdle which limits the application of TiO_2 in photocatalytic hydrogen production is the fast recombination of its photogenerated electron and holes and its inability to utilize the visible radiation. Noble metal loading (Au, Ag, Pt etc) is one of the routes employed for sensitizing TiO_2 and has proved in significantly enhancing the photoactivity of TiO_2. The underlying mechanism being that the Fermi level of the metal is lower than TiO_2 and hence there can be an electron transfer from the conduction band of the semiconductor to the metal [1]. This consequently leads to significant reduction in the

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recombination of photo generated electrons and holes which is reflected in enhanced photocatalytic activity. However, the amount of noble metal loaded is crucial as excess of noble metal can lead to a decrease in photocatalytic activity mainly because it may hamper the photon absorption of TiO_2 and block its active sites. Moreover, at higher loadings, the noble metal may itself act as a recombination centre for photo generated electrons and holes further affecting the efficiency.

With the advent of nanotechnology and nanoscience, these noble metals particularly Au in its nano form (AuNPs) has shown tremendous potential. The ability to tailor the shape, size and morphology of these nanoparticles make them attractive candidates for development of visible light active photocatalysts. Recently, the enhancement of photocatalytic activity by noble metal particles has been explained by the phenomenon of Surface Plasmon Resonance (SPR). SPR is a phenomenon where collective oscillations of valence electrons take place on account of the incident photons. When the frequency of incident light matches with the frequency of surface electrons oscillating against the restoring force of positive nuclei, it leads to a resonant condition. In case of nano structures, the phenomenon is called as LSPR (Localized Surface Plasmon Resonance). It is now known that SPR has a significant role to play in photocatalytic reactions involving semiconductor and a plasmonic metal nanostructure. These plasmonic noble metal nanoparticles can significantly enhance the rate of photocatalytic activity by their ability to concentrate the UV–vis radiation and by increasing the energy of photo generated charge carriers [2].

Recent literature reports are inundated with AuNPs and their loading on various supports for their possible application in the field of heterogeneous photocatalysis, fuels cells and sensors [3–7]. Chen et al. reported the application of Au/TiO_2 in methylene blue dye degradation as well as in photocatalytic water splitting [8]. Tanaka et al. reported Au/TiO_2 prepared by multi step photo deposition process in hydrogen production from 2-propanol, ethanol and ammonia in aqueous solutions [9]. Kominami et al. [10] reported that Au nanoparticles supported on CeO_2 showed better photocatalytic activity than Au loaded on TiO_2 in mineralization of organic acids. However, Au/Ceria has been mostly reported for oxidation reactions or in water shift gas reaction and rarely reported for photocatalytic splitting of water. Cu_2O has a potential in solar hydrogen production due to its visible light absorption as its band gap is in the range of 2.2–2.3 eV. Au–Cu_2O has also been reported [11–13]. Although several reports are available on Au nanoparticles supported on various metal oxides, very few have proved to be efficient in photocatalytic splitting of water and even fewer are reported for their efficient catalytic activity in both UV as well as in visible range from the point of view of solar energy utilization. In the present investigation, two UV active (TiO_2 and CeO_2) and two visible active (Cu_2O and Fe_3O_4) metal oxide supports were chosen for study. We synthesized Au/TiO_2, Au/CeO_2, Au/Cu_2O and Au/Fe_3O_4 and studied their photocatalytic properties in water splitting reaction. The noble metal was photo deposited on each of the metal oxides. Au/TiO_2, Au/CeO_2 and Au/Cu_2O show better photocatalytic activity than TiO_2, CeO_2 and Cu_2O alone. The role of SPR effect in enhancing the photocatalytic activity was investigated.

2. Experimental

2.1. Materials and method

Titanium dioxide was procured from Degussa P-25, commercially available Cerium oxide and copper oxide, ferrite and Gold chloride was procured from Merck and ethanol used was from Decon Lab. All the chemicals were used as such without any further purification.

2.2. Characterization

Diffuse reflectance spectroscopy measurements were carried out on Cary 500 scan UV–Vis–NIR spectrophotometer operating in air at room temperature. $BaSO_4$ was used as the reference material. Powder XRD analyses of the samples were recorded on Scintag-XDS-2000 spectrometer with Cu K α radiation with applied voltage of 40 kV and current of 40 mA. TEM micrographs were recorded on Phillips CM100 electron microscope operating at 100 kV. The TEM samples were prepared by directly drop casting the samples on carbon coated Cu grids.

2.3. Photocatalytic hydrogen evolution experiments

2.3.1. Rapid screening

The photocatalytic activity of the photocatalysts was evaluated for hydrogen production through rapid screening. In a typical experiment, a known amount of photocatalyst was taken in 40 mL glass vial and to it 19 mL of water was added. Ethanol (1 mL) was added as a sacrificial donor. The vial was properly sealed and evacuated. The reaction mixture was then illuminated under UV–vis radiation source (tungsten lamp) for 2 h. The evolved gas was analysed on a gas chromatograph.

2.3.2. Online evaluations

The photocatalytic experiments were carried out in a glass enclosed reaction chamber with a quartz inner radiation reaction vessel. The glass chamber was connected to a gas circulation evacuation and water cooling system. In a typical experiment, 100 mg catalyst, 322 mL distilled water, and 18 mL ethanol were taken in the glass reactor with a magnetic stir bar. The reaction mixture was evacuated and filled with Ar five times to remove all the dissolved gases. This was followed by irradiation using a 450 W high pressure Hg lamp via a quartz tube. Water at 20 °C was circulated continuously through the outer walls of the reactor and the quartz vessel to make sure that the temperature of the reaction mixture did not exceed 35 °C. The activity of these catalysts for water splitting was investigated for 10 h irradiation period, using a fresh catalyst each time. 2 M $NaNO_2$ solution was used as a filter to cut off UV radiation during studies under visible light ($\lambda > 400$ nm). H_2 production was monitored using an online GC system (GOW-MAC 580