

# Mesoporous Nickel Silicate@gold Nanoparticles: An Excellent Plasmonicphotocatalyst for Photo-Generation of H<sub>2</sub> by Visible Light

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Article Info Volume 82 Page Number: 2377 - 2383 Publication Issue: January-February 2020

Article History Article Received: 14 March 2019 Revised: 27 May 2019 Accepted: 16 October 2019 Publication: 18 January 2020

#### Abstract

Mesoporous silica has drawn attention as a substrate for varieties of photocatalytic systems because ofhigh area of surface as well as transparency towards visible light. Herein a novel core-shell structured plasmon modified nickel silicate photocatalyst has been synthesized over mesoporous silica. The photocatalyst has been well characterized through P-XRD, scanning electron microscopy,EDX spectroscopy, X-ray photoelectron spectroscopic techniques. The as synthesized material shows excellent evident light sourcecompelled with hydrogen generation contrary to neat material. An enhanced photocatalytic hydrogen evolution can be attributed to surface modification using mesoporous silica along with plasmonic gold nanoparticles presence which enhances visible light absorption efficiency through LSPR effect.

Keywords: core-shell structure, H2 production, LSPR effect, mesoporous silica.

#### I. INTRODUCTION

The pioneering work of Fujishima and Honda on photocatalytic hydrogen evolution in 1972, ushered photocatalysis to be the most sought after method towards green generation of clean H<sub>2</sub> fuel in current research [1]-[5]. In this regard, TiO<sub>2</sub> has been aencouraging photocatalyst among semiconductors for the photocatalytic reactions due to its high efficiency, good stability and low toxicity [6]-[7]. However, the insufficient utilization of solar spectrum (only UV light) opens the door for alternative semiconductor photocatalysts i.e. WO<sub>3</sub>, Ag<sub>3</sub>PO<sub>4</sub>, CdS, BiVO<sub>4</sub> as

well as modification with different noble metal nanoparticles [8]-[16].

Noble metal NPs into semiconductor photocatalysts have been integrated to enhance their photocatalytic efficiency via SPR phenomenon [17]-[19]. The evident light inducedcollective oscillation of free electrons leads to SPR effect when the oscillation frequency of light induced

Electromagneticfield. Among various plasmonic metals, Au has received utmost attention due to its unrivalled stability in different reaction conditions i.e. metal leaching, over-oxidation as well as highest selectivity for various photocatalytic



reactions [20]-[21]. To overcome the agglomeration, enhance the stability and catalytic activity, Au NPs have been anchored onto various metal oxides, silica as well as various polymers as support which is used to increase area of the surface the increases the specific surface area as well as partingefficacy for reuse. For this purpose, Au NPs has been fabricated over  $TiO_2$  and ZnO to enhance their photocatalytic activity [22]-[23].

Metal silicates have been widely used for energy storage, adsorption, separation and catalyst support due to their thermal and chemical stability, low cost and highly porous structures [24]. Herein we have considered nickel silicate as a catalyst support to investigte the plasmonic effect of Au NPs.Modified Stobber method has been used to synthesize spherical silica nanoparticles as core for nickel silicate and has been etched in the subsequent step. Au NPs have been decorated over nickel silicate surface by urea reduction method. The photocatalyst shows photocatalytic hydrogen evolution excellent through liquidexcruciatingresponse. The effect of plasmonic Au NPs isthoroughly discussed.

#### II. EXPERIMENTAL

#### A. Materials

Analytical grade tetraethyl orthosilicate (TEOS), Nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O), Urea, Sodium hydroxide (NaOH), (3-Aminopropyl)triethoxysilane (APTES), Gold chloride (HAuCl<sub>4</sub>), absolute ethanol (EtOH) and ammonium hydroxide (NH<sub>4</sub>OH) were procured from Merck India. Deionized water has been used throughout the reactions.

## B. Synthesis of Silica Nanoparticles

Modified Stobber's method [25]has been implemented for the synthesis of silica nanoparticles. According to this method, a homogeneous mixture of 25% NH<sub>4</sub>OH and deionized water and absolute ethanolwas prepared under vigorous stirring. 25ml of TEOS isintroduced in studied mixture and aged at ambient condition for almost full day. Subsequently, with the help of ethanol, the colloidal solution is centrifuged, cleaned and dried in oven at 100' C temperature for 12 h.

## Synthesis of Mesoporous Nickel Silicate@ Gold Nanoparticles

In a typical procedure, the as synthesized silica nanospheres were dispersed in the deionized water. To this solution a suitable amount of Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was added and stirred for 30 minutes followed by addition of urea and fluxed again at 95 °Centigrade for only 4 h. Then the colloidal solution is etched with 0.5 M NaOH for full day. The final solution was then centrifuged and washed to remove undesirable particles denoted as m-SiO<sub>2</sub>@NS. The as synthesized nickel silicate was loaded with Au NPs where gold nanoparticles have been fabricated by urea reduction method [26] followed by calcination at 450 °C for 4h denoted as m-SiO<sub>2</sub>@NS@Au NPs. The detailed synthesis procedure has been depicted in Scheme-1.



Scheme 1. Illustrating the syntheticmethod of m-SiO<sub>2</sub>@NS@Au NPs.



# C. Photocatalytic water splitting reaction

Photocatalytic hydrogen evolution through water splitting reaction is doneby dispersing 21 milligram of the substance in 20 mL of 10 vol% triethanolamine (TEOA) solution in a 100 millilitre, where TEOA act as hole scavenger.A Xenon lamp is used as a light source. According irradiation, solution was purged with nitrogen and stirred for 15 minutes forhomogeneous dispersion of the photo catalystand removal of dissolved gas. The evolved gas wasanalysedto be hydrogen with the help ofgas graph mountedon a thermal detector.

# III. CHARACTERIZATION

"A RIGAKU MINIFLEX X-ray diffractometer having Cu Ka (l=1.54 Å)"as irradiation source has been utilized for analyzing the structure related to crystal of the synthesized material within the range 20° to 80°. Field Emission Scanning Electron Microscopeconnected with X-ray spectrometer was employed for analyzing photo catalyst microstructure. An XPS of the photocatalysts has been accomplishedby utilyzingaMg Ka source attached Kratos Axis 165 instrument. The catalyst photocatalytic activity has is exploring towards liquidexcruciatingresponse to produce hydrogen.

# IV. RESULTS AND DISCUSSION

# A. Crystal Structure

The study of X- ray diffraction has been performed for exploring crystal structure. The pattern of XRD m-SiO<sub>2</sub>@NS@Au NPs shows the characteristic diffraction peaks of Nickel silicate (JCPDS card no.- 43-0664) as well as Au NPs. The peaks in fig. 1 observed at  $2\theta$ = 26.09°, 34.09°, 41.82° and 60.40° are indexed to (103), (110), (200) and (300) peaks of nickel silicate [27]. The deflectionheights detected at  $\theta_2$ = 39.04°, 43.98°, 54.55° and 67.26° are indexed to (110), (201), (222) and (312) planes of Aurum(Au) NPs [28]. The crystallinity of Au NPshas been signified with the most intense peak observed at  $38.04^{\circ}$ .

# Fig. 1. Deflection of X-rayof m-SiO<sub>2</sub>@NS@Au NPs showing the height of NiO<sub>3</sub>Si and Au NPs.

# B. Morphology Study

The FESEM is used for studying the morphology of as synthesized nickel silicate@ Au NPs samples [29], wherein FESEM is field emission scanning electron microscopy. The figures from the fig. 2a-c demonstrate the removal of Au NPs of nickel silicate surface. The energy dispersive X-ray spectrum has been represented in fig. 2d which indicates the presence as well as successful incorporation of Au NPs on the nickel silicate surface.



# Fig.2. (a-c) FESEM images at different magnifications and (d) Energy dispersive X-ray spectrum of m-SiO<sub>2</sub>@NS@Au NPs representing the occurrence of Ni, Si, Oxygen and Aurum.

# C. Analysis of chemical state

The oxidation state and its electronic environmentexisting in photocatalyst has been analyzed through "X-ray photoelectron spectroscopy" [30]. The XPS (fig. 3a) consists of Carbon, Si, Ni and O which links to the successful synthesis of the catalyst. The core level peaks were deconvoluted through CASA XPS software package to study the oxidation states of the



elements. Maximum level at 283.7 eV for core level of carbon first state has been considered as the reference for analysis (fig. 3b). There are two maximum level at 102.8 eV and 98.9 eV were obtained by the deconvolution of the core level of Si 2p (fig. 3c) which are attributed to the characteristic peak of silicates and silicon respectively [30]. The deconvolution of Ni 2p core level gives rise two set peaks for 3p 3/4 and 3p 1/4 (fig. 3d) and heights at 853.8 electronVolt and 871.5 electronVolt are attributed to the  $Ni^{2+}$ oxidation states of nickel silicate along with two satellite peaks observed at 859.6 eV and 877.6 eV respectively [30]. As revealed from the fig. 3e,O 1s core level spectra and connected with two distinct peaks at 530.7 eV and 532.3 eV that is ascribed to Ni-O linkage and Si-O-Si bonding in nickel silicate respectively [30]. The lack of distinct Au peaks in fig.3f.





#### D. Photocatalytic Activity

Below the radiation of evident light (where  $\lambda$ >420 nm), the photocatalyst is tested for water

splitting reaction. In a detailed procedure, used just triethanolamine (TEOA) was as holescroungerof 20 mg of the photocatalyst[3]. The photocatalyst was able to produce 130 µmolh  $^{1}$  H<sub>2</sub> which is 5 times more than the parent under visible counterpart (fig. 4a) light illumination. Furthermore, fig. 4b shows the stability of the catalyst for 3 consecutive cycles. The effect of catalyst dosage and different scavengers on photocatalytic hydrogen generation reaction was tested and represented in fig. 4c and 4d respectively. The dosage test was carried out with various catalyst amount ranging from 20 mg to 500 mg and no significant change was witnessed with catalyst amount above 50 mg. The scavenger test was performed to scavangee, h<sup>+</sup>  $OH^{-}$  and  $(\bullet O^{2-})$ , by using a mixture of silver nitrate, TEOA [8]. From the results, photocatalytic H<sub>2</sub> production was carried out by electrons as the major active species. The following equation was used to calculate the apparent quantum yield (AQY) for photocatalytic water splitting reaction and found to be 2.8%.:

 $AQY (\%) = \frac{2 \times Number of H_2 molecules}{No. of photon absorbed} \times 100$ 



Fig. 4. (a) Rate of H<sub>2</sub> evolution over m-SiO<sub>2</sub>@NS and m-SiO<sub>2</sub>@NS@Au NPs, (b) stability curve, (c) effect of catalyst dosage and (d) consequences of various searchers on the photocatalytic H<sub>2</sub>development by m-SiO<sub>2</sub>@NS@Au NPs.



Based on the photocatalytic generation of H<sub>2</sub> by photocatalyst, a probable phenomenon issuggested orillustrated in Scheme 2. Upon irradiation of evident light, photo-excited e are upper band of nickel transferred to the silicateleaving behind the holes in the lower band, wherein the upper ban is conductance band and the lower band is valence band. Meanwhile, metallic electrons in Au NPs are excited above the Fermi level due to SPR effect and addedin the upper band of the nickel silicate support. Then formation of a layer related to space charge at the interface increases separation of the Au-NS carrier which is already charged and thereby its recombination [31],[32]. reducing The photocatalytic activity of the synthesized catalyst is enhanced by increasing the lifetime of these carriers. So the molecular mechanism of photocatalytic activity is as follows:

> $NS + h\nu \rightarrow NS(e_{CB}^- + h_{VB}^+)$  $Au + h\nu \rightarrow Au^+ + e^-$

$$NS \ (e_{CB}^-) + 2H^+ \rightarrow H_2$$



## Scheme 2. Plausible mechanism of H<sub>2</sub> evolution over m-SiO<sub>2</sub>@NS@Au NPs.

## CONCLUSION

A novel core-shell structured plasmon modified nickel silicate photocatalyst has been synthesized over mesoporous silica. The catalyst absorption efficiency has been enhanced with loading of plasmonic Au NPs.The photocatalyst has been well analyzed through PXRD, SEM, EDX and XPS techniques. The photocatalyst has been able to produce 130  $\mu$ molh<sup>-1</sup> H<sub>2</sub> through evident source of light persuadedliquidexcruciating reaction. Theplasmonic gold nanoparticles enhances the visible light absorption efficiency through LSPR effect is liablefor enhanced photocatalytic hydrogen evolutionas well as the surface modification using mesoporous silica. This work demonstrates anrational design for morphology oriented synthesis of m-SiO<sub>2</sub>@NS@Au NPs as an excellent photocatalyst towards evident source of light compelled photocatalytic liquid excruciating response.

#### ACKNOWLEGDEMENT

All authors acknowledgeSiksha 'O' Anusandhanfor laboratories and infrastructural facilities.

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