ABSTRACT

Phenolphthalein (phph) immobilized gold nanostructures (phph-AuNSs) within different pH 1-12 are prospective for chemical sensing. Metallic nanoparticles are preferred over oxides due to non-toxicity, excellent structural, and optical properties. This paper reports the different shapes and sizes of sol-gel derived phph immobilized Au nanoparticles by varying the pH values. Microscopic analysis revealed the dimensions and shapes (dendrites, flower and spherical) of the phph immobilized gold NPs matrix. FTIR spectra displayed the bonding vibration of AuNPs in the presence of phph species. The sensor response is optimized at basic pH 12 with 9.9 pKa value at 555 nm.

1. INTRODUCTION

Over the past decades, metal-based nanoparticles i.e., gold nanoparticles physical, chemical, biocompatible and optical properties have attracted extensive research interests towards promising applications such as photothermal therapy (Wan et al. 2016), bioimaging, nanomedicines, drug delivery, catalysis, nanoelectronics, photonic and plasmonic devices fabrication and sensors (Chaudhary et al. 2015). Spherical and non-spherical gold nanocrystals with specific shapes including wires, rods, prisms, polyhedra, nanocages, flowers, and dendrites can be synthesized by different methods like seeded growth method (Sara et al. 2008, Ziegler et al. 2011), pulsed laser ablation (Kabashin et al. 2003), pulsed laser ablation in liquid (Wan et al. 2016).
2016), chemical method (Maruyama et al. 2015), and many more. Among them, gold dendrites have been attracting interest in catalysis, sensing, and surface-enhanced Raman scattering (SERS). Extensive efforts have been dedicated to obtaining the rational control over the morphologies of the materials. Therefore, in modern materials physics and chemistry, is still a challenging goal to manipulate the morphology, size, and size distribution of metal-based opto-chemical materials. In the sol-gel based synthesis of nanoparticles, pH is an important parameter which shows obvious impacts on the rates of precursor conversion leads to nucleation and growth of nanoparticles. So, the pH effects on the morphology/particle size of phenolphthalein immobilized gold NPs were investigated at room temperature.

2. EXPERIMENTAL

2.1. SYNTHESIS OF THE SOLS

The gold source precursor i.e., HAuCl4 (0.406 mmol) was dissolved in the mixture solution of 20 ml of isopropanol and 2ml of HCl. Afterward, 1ml of 0.0005M of PEG was added in the mixture under constant stirring. The reaction mixture was stirred and heated at 70 °C for 1 hr, and then Au sol was let to cool at room temperature. After aging for 24 hrs, 1 ml of 0.005M phenolphthalein (phph) was added in the Au sol. phph encapsulated Au matrix sol was obtained after 1 hr stirring at room temperature. The prepared sols were aged at room temperature for several days. The pH of phph encapsulated Au matrix sol from 1-12 was adjusted by mixing of HCl and NaOH solution.

3. CHARACTERIZATION

The morphology of phph immobilized gold NPs was analyzed using an optical microscope (AmScope). The size distribution and average diameter of phph-AuNPs were determined by J image. FTIR spectra were recorded using a Perkin-Elmer spectrophotometer (Luminescence LS55) within the range of 650cm⁻¹-4000cm⁻¹. The absorption spectra of phph immobilized gold NPs within different pH solutions were measured by USB4000 spectrometer in the range of 400 to 650 nm. The solutions were placed in a quartz cuvette (12.5 × 12.5 × 45 mm³) and inserted in the cell holder. While white light was used as a light source.

4. RESULTS AND DISCUSSION

The optical micrographs of phph immobilized AuNPs’s shapes within different pH solutions 1, 5, 7, 10 and 12 as shown in Fig. 1(a-e), respectively. A dense uniform layer of spherical nanoparticles was observed at pH 1 [Fig. 1(a)] with an average diameter of 0.17 µm ± 0.09 µm [Fig. 1(f)]. While phph immobilized gold dendritic were observed at pH 5 [Fig. 1(b)] with an average length of 2.68µm ± 0.9 µm [Fig. 1(g)].
Fig. 1 Optical micrographs of phph immobilized gold NPs’s shapes (a) pH 1, (b) pH 5, (c) pH 7, (d) pH 10, (e) pH 12. Whereas, (f-j) corresponding to the diameter of particles and length of dendrites of (a-e), respectively.
Probably, when pH 5 interacted with phph immobilized gold NPS, a complex was formed immediately via electrostatic interaction and van der Waals interaction between the positively charged head groups of PEG and the negatively charged AuCl\textsubscript{4} ions, which self-assembled into dendrites (Junyan et al. 2011). With pH increased up to 7, the length of the dendrites changed into hyper branched sheaf-like structures [Fig. 1(c)] and observed an average length was 1.13 \( \mu \text{m} \pm 0.66 \mu \text{m} \) [Fig. 1(h)], ascribed to the splitting phenomenon of crystals as reported by other researchers (Guanjun et al. 2012). When the pH increased up to 10, the shape of phph immobilized gold particles became pseudo-spherical [Fig. 1(d)] with average diameter 1.26 \( \mu \text{m} \pm 0.78 \mu \text{m} \) [Fig. 1(i)]. However, spherical NPs were observed at pH 12 [Fig. 1(e)] with average diameter of 0.99 \( \mu \text{m} \pm 0.43 \mu \text{m} \) [Fig. 1(i)]. The micrograph inspection suggested that dense spherical morphology was changed into dendritic shapes first and then it gradually changed into dispersed spherical particles by increasing the pH from 1-12. Thus, it confirmed that phph immobilized gold NPs shape/morphology was strongly dependent on pH.

![FT-IR spectra of phph immobilized gold NPs within different pH solutions](image)

Fig. 2 FT-IR spectra of phph immobilized gold NPs within different pH solutions

A small band \( \sim 877 \text{ cm}^{-1} \) in all samples [Fig. 2] belongs to the H\text{AuCl}_4 ions, as documented in the literature (Santhoshkumar et al. 2017). The little intense band \( \sim 1043 \text{ cm}^{-1} \) is corresponding to C=O stretching in pH 1, pH 5, and pH 7 but it vanished in pH 10, and pH 12 samples, suggested the dissociation of functional groups on the surface of the gold particles; consequently, changes in the pH leads to the variations in size and shapes of gold NPs which also observed in microscopy. The sharp band \( \sim 1637 \text{ cm}^{-1} \) is attributed to the stretching of C=O carbonyl functional groups from PEG and phph species within gold NPs. The bands at 2115 cm\textsuperscript{-1} are indicative of PEG
presence in all samples, corresponding to the symmetric and asymmetric stretching vibrations of the CH$_3$ and CH$_2$. The broad band around 3300 cm$^{-1}$ corresponding to the stretching of O-H groups [9].

![Absorption Spectra](image1)

**Fig. 3 (a)** absorption spectra of phph immobilized gold NPs within different pH solutions, **(b)** pKa value at 555 nm

Fig 3(a) shows the absorption spectra of phph immobilized gold NPs in the pH solution of 1, 5, 7, 10, and 12. There is no band is detected for pH 1 and 5, however, after increasing pH up to 7, a notable absorption band is observed at 596 nm. By increasing the pH 10 and 12, it induced a blue shift from 596 nm to 555 nm accompanied by an increase in absorption intensity. The peak shifts to the blue wavelength around 555 nm is probably due to inter-band transitions as documented in our previous studies (Wan et al. 2016). Moreover, the pKa value is found to be 9.9 at 555 nm as shown in Fig. 3(b), indicated a smaller degree of dissociation at any given pH medium.

**5. CONCLUSIONS**

phph immobilized gold nanostructures/nanoparticles (phph-AuNPs) within different pH solutions i.e., 1, 5, 7, 10 and 12 were synthesized by a sol-gel method for chemical sensing. Different shapes of phph immobilized gold nanoparticles from aggregated spherical to dendrites and then dispersed spherical NPs were observed at pH 1, pH 5 and pH 12, respectively. FTIR analysis confirmed the bonding vibration of gold NPs with functional groups of PEG and phph. Moreover, the pH value affected the dissociation of functional groups and resulted in the variations of gold NPs size and shapes. Sensor response was optimized at pH 12 with 9.49 pKa value at 555 nm by absorption analysis.

**REFERENCES**


