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Optical sensing of carbon dioxide based on colloidal gold nanoparticles

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ABSTRACT

Gold nanoparticles, owing to their fascinating optical properties, are considered very attractive for detecting devices. Size, shape as well as surrounding environment may affect the sensing behavior of nanomaterial and thus the study of such factors is of great importance. We investigatedthe gas sensing performance of colloidal gold nanoparticles of different sizes in carbon dioxide gaseous environment by measuring the optical behavior with and without gas. The citrate reduction method was adopted to synthesize gold nanoparticles; scanning electron microscopy was used for morphological studies while optical properties were determined by spectroscopic ellipsometery. We observed a size dependent decrease in the transmission spectra of colloidal gold nanoparticles in the presence gaseous environment.

1. INTRODUCTION

Gas sensing technology is achieving more and more importance and attraction due to its increasing demand in various fields such as industry to detect different gases e.g., methane in mines and polluting gases from vehicles; medical applications and health e.g., monitoringof carbon monoxide and other dangerous gases and measuring of greenhouse gas for environmental studies (Liu 2012).
Optical gas sensors, which are based on measuring the optical properties of sensing materials in the absence and presence of the target gas,are getting much attention than other gas detectors including electrochemical and semiconductor gas sensors by showing less response time, insignificant drift and high gas specificity, with negligible cross response to other gases. Thus optical gas sensing provides low-cost sensors with good performance and high end laboratory equipment. Thus their higher sensitivity, selectivity and stability make them promising for practical applications (Hodgkinson 2013).
Over last few decades, with dawn of nanomaterialsthis field of gas detection has

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become more striking due to extraordinary surface to volume ratios of nanomaterilasand their higher sensitivity to surface interactions. Industrial interest is growing remarkably in this arena to develop a class of sensing devices with greater sensitivity and operational range utilizing this enhanced sensitivity of nanoscale materials. The factors which may influence the sensing behavior of nanomaterial include size, shape as well as surrounding environment. Therefore, for the fabrication of practical optical sensing devices these parameters need to be studied in detail (Dobrokhotov2006, Shah 2012, Dairo 2009).

Gold nanoparticles, because of their fascinating photosensitive properties, are being studied as the promising applicants for optical sensing devices. In different ways gold nanoparticles are employed to investigate the detection of various target gases. In most cases, gold nanoparticles are used in combination with other materials for example Sadek et al (Sadek 2010) used highly dispersed gold nanoparticles of diameter 5 nm and 10 nm supported on nitrogen doped multi-walled carbon nanotubes for hydrogen sensing. They achieved the highest sensitivity of the target gas with smaller size of the particles.Similarly gold nanoparticles were also successfully utilized for functionalizing the Gallium nitride (GaN) nanowires to study the response of Argon (Ar), Nitrogen (N_2) and methane (Dobrokhotov 2006). Young et al (Young 2012) reported that sensitivity of carbon nanotubes based ethanol gas sensors could be significantly enhanced by adsorption of gold nanoparticles. The effect of different profiles (dot and rod-shaped) of gold nanoparticles for the sensing responses towards different kinds of alcohol vapors (ethanol, methanol, isopropanol and gases suchas NH_3)) with TiO_2 thin films investigated by Manera et al (Manera 2008) and an increased in the optical absorption in case of nanocomposite (TiO2/Au) thin films was recorded than only TiO_2 thin film. This trend was found simmilar for all investigated vapors; however no significant effect of particles shape was noticed. The detection of trinitrotoluene (TNT) was also investigated by immunosurface modified with gold nanoparticles and it was found that the observed sensing performance was four times higher than that without gold nanoparticles (Kawaguchi 2008).

Gold nanoparticles are also used as gas sensors by functionalizing the surface of the particles with some other materials such as polymers or molecules with different functional groups. For example, biofunctionliedcolloidal gold nanoparticles were successfully used to for the detection Hydrogen sulfide (H_2S). It was argued that sensing perform is due to the bio-moieties on the particles which have higher dielectric constant. It was also noted that sensing performance of gold nanoparticles was better than other solid state H_2S sensors (Ganachari 2011). Zhang and co-worker functionalized the gold nanoparticles with OH and CH_3 terminal groups for investigate the vapor sensing performance of dichloromethane (DCM), methane and ethanol (Zhang 2002). They conclude that gold nanoparticles can be utilized for the detection of polar and non-polar molecules depending upon the functionalizing terminal group of the gold nanoparticles. Very recently Ma and Yung (Ma 2014) functionalized gold nanoparticles with a specially synthesized polymer for the detection of dissolved carbon dioxide ($dCO_{2)}$.The sensing mechanism based on the color change of gold nanoparticles solution due to the aggregation of colloidal gold in the presence of dissolved CO_2. Still, there is a need to explore simple and easy approaches to study the optical sensing characteristic of nanoparticles which could lead to devices

fabrication.

We, in this work, adopted a facile method to study the gas detecting performance of colloidal gold nanoparticles. We used carbon dioxide (CO_2) as target gas. Spherical gold nanoparticles of different diameters (size) were synthesized by reducing hydrogen tetrachloroaurate ($HAuCl_4$) with tri-sodium citrate in water. To determine the surface morphology and size scanning electron microscopy (SEM) was used.The gaseous environment was introduced by passing the gas through the colloidal gold solution. Optical characteristics of colloidal gold nanoparticles with and without gas flow were measured by spectroscopic ellipsometery. We recorded a decrease in transmission spectra of gold nanoparticles in the presence of gaseous atmosphere. We also noticed a size dependent sensing behavior of gold nanoparticles for CO_2 gas.

2. EXPERIMENTAL DETAILS

All the reagents were of analytical grade and the highly purified water was used throughout the experimentSpherical gold nanoparticles of three different sizes (diameters)were synthesized following the citrate reduction approach (Raza 2011, Brown 2000). First smaller (seed) gold nanoparticles were prepared and then these seeds were grown into larger particles

For smaller gold nanoparticles (sample A), 100ml of 1mM HAuCl4was heated to 100°C under refluxing conditions and then 10ml of 38.8mM Sodium citrate ($Na_3C_6H_5O_7$)was added at once into the boiling aqueous solution while stirring vigorously. A color change originally from yellow to transparent, to dark blue and finally, after about 2 mints, to burgundy red which was an indication of completion of the reaction.

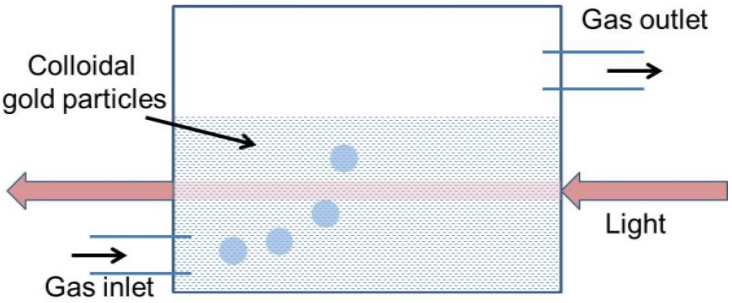

Fig.1The set-up to produce gaseous environment for optical gas sensing of gold nanoparticles

For medium size gold nanoparticles (sample B), 5ml of seedcolloids were added simultaneously with 430µl of38.8mM Sodium citrate (final concentration 0.17 mM)into a 92.5ml boiling solution of 0.3mM $HAuCl_4$stirring continuously under refluxing environment. Similarly for larger gold nanoparticles (sample C), 100ml of 0.3mM $HAuCl_4$was heated up to boiling with continuous stirring and then 443µl of38.8mM Sodium citrate (final concentration 0.17 mM)and 1ml of seed particles were addedat

once under refluxing condition. The heating with stirring was continued for further 10-15 min before cooling down to room temperature

To determine the morphology and size of the prepared particles, scanning electron microscopy was used. All three size gold nanoparticles were deposited of silica substrates by functionalizing the silica surfaces with (3-Mercaptopropyl) trimethoxysilane (MPTMS, $C_6H_{16}O_3SSi$). MPTMS acted as a binding agent between silica and gold particles providing a high affinity for gold particles due to its thiol end groups (Raza 2011).

Optical gas sensing properties of colloidal gold nanoparticles were investigated by measuring the transmission spectra in the absence and presence of gas flow with a variable angle spectroscopic ellipsometer (VASE J. A. Woollam) in the photon energy range 0.8–4.5 at a fixed zero incident angle with respect to the surface normal. CO_2 were used in this work, the gaseous environment was produced by passing the gas flow through the colloid in a transparent chamber as shown in figure 1.

3. RESULTS AND DISCUSSION

In order to determine the surface morphology and size of the prepared entities bY SEM, colloidal particles were deposited on the silica substrates by derivatizingthe silica surfaces with MPMTS. In figure 2, SEM images of all three types ofAuNPs; smaller, medium and larger size are presented in (a), (b) and (c) respectively. The measured particle diameters were found 13 ±5nm (colloid A), 25 ±3nm (colloid B) and 45±5nm (colloid C). The insets show the corresponding colloidal gold solutions for each sample as indicated on each vial.

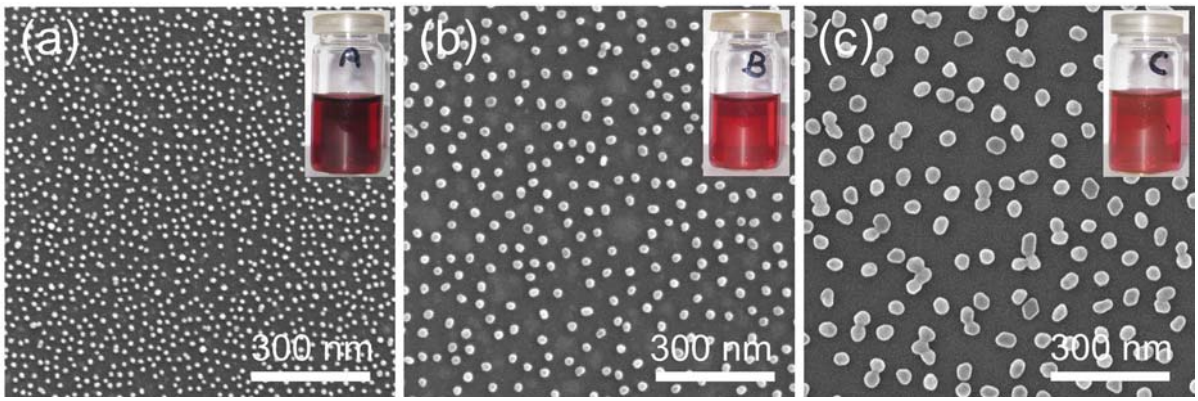

Fig.2SEM micrographs of gold nanoparticles deposited on silica substrates: (a) smaller diameter 13nm (colloid A), (b) medium size 25 nm (colloid B), and larger diameter particles 45 nm (colloid C). Insets show the colloidal gold solution of each sample.

As can be seen in figure 2, all AuNPs are nicely and randomly adsorbed on the silica substrates. The reason of this random deposition of nanoparticles is thatgold nanoparticlesin the solution werestabilized by citrates and thus AuNPsexperience a short-range repulsion due to the negative charge of citrates while the exposed

thoilgroups of MPTMS on the substrates provide the irreversible bindingcausing the nanoparticles immobile as they were attached to the thiol groups. The most of the particles in figure 2(a) and (b) having smaller and medium diameters are of almost spherical geometries. However, some of larger particles seem differing from the perfect spherical geometries. Perhaps with the increase of the particle size, the profile of the growing particles was likely affected by the preferential growth on crystalline faces which created the irregularities forming elongated or slightly protrudedshapes

The optical characteristics of all colloidal gold nanoparticles without and with gaseous environment are shown in figure 3. The CO_2gas detecting performance of smaller gold nanoparticles (colloid A) is demonstrated in figure 3(a). The transmission spectra measured by spectroscopicellipsometery without (black solid line) and with (dashed red line) CO_2 gas flow through the solution shows a clear fall in the trasnmision in the case of CO_2gas. Similar CO_2gas sensing activity were also found with other medium and larger gold nanoparticles as depicted in figure 3(b) and (c) respectively. However, smaller gold nanoparticles were found showing highest sensitivity for CO_2as compared to medium and larger particles (figure 3 (d)).

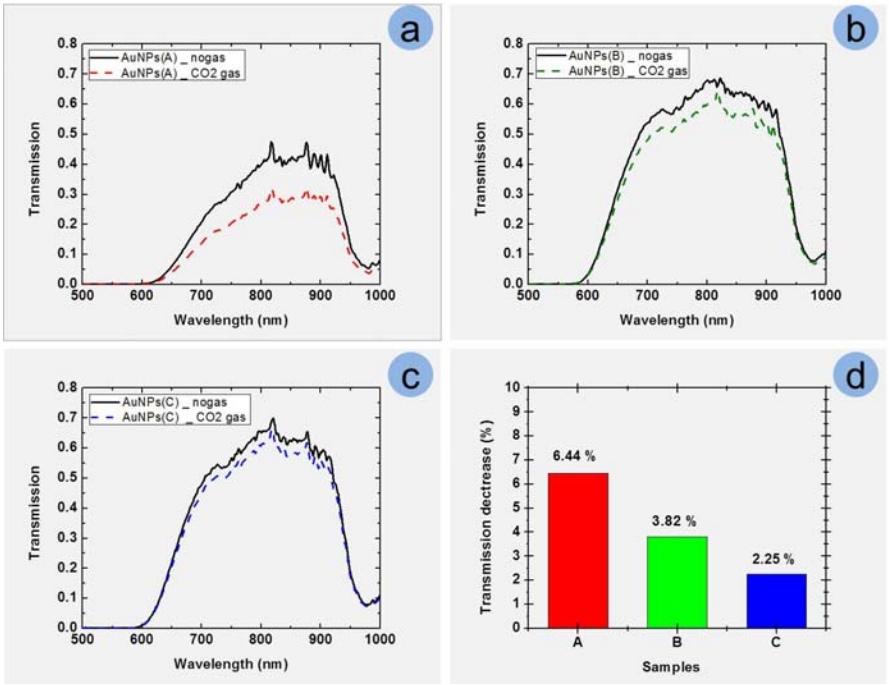

Fig.3The experimentally measured optical transmission spectra of colloidal gold nanoparticles with and without CO_2 gas flow. In all three cases; (a) 13nm smaller,(b) 25nm medium, and (c) 45nm diameter larger nanoparticles, a decrease in transmission in presence of CO_2 gas is evident. The effect of particle size on this trend is in shown in figure 3(d)

There could be numerous factors which may influence the optical properties of the materials for example in case of semiconductors optical behavior depend on the energy band gap and band gap is very sensitive to temperature, radiation effect, grain

boundaries, doping, three dimensional quantum charge size effects, and composition change (Siraj 2013, Riaz 2009, Saeed 2013). However in the case of metallic nanoparticles such as gold and silver, mostly 'surface plasmon resonance (SPR)' is considered responsible for the optical characteristics. Actually, when a light with wavelength greater than that of nanoparticle size shines on them and if the natural frequency of the nanoparticle surface electrons matches with incident light frequency, the standing resonance conditions can be set up. As a result, the mobile electrons at surface of the particle start to oscillate against the restoring force of positive nuclei resulting in the electron density polarization. The 'surfaces plasmon resonance' is the collective oscillation of these surface electrons in resonance with incident light frequency (Link 2000).

The absorption and scattering spectroscopy can be used to determine the resonance condition while parameters such as the shape, size and the dielectric constants of both the metal and the surrounding medium can significantlyaffect this condition. Achange in the electric field density on the surface can be activated by the variation in size and shape of nanoparticles which results in a modification of the oscillation frequency of the electrons resulting in a change in cross-section for the optical behavior including absorption and scattering.The variation in size and shapeof nanoparticles can cause a shift in the electric field density on the surface which results a modification in the oscillation frequency of the electrons and thus cross-section for the optical performance including absorption and scattering may change. Likewise, the surrounding material can affect dielectric constant which can directly influence surface ability to accommodate the electron charge density and consequently oscillation frequency can be changed(Eustisa 2006).

The mechanism of CO_2-gas induced optical transmission change can be ascribed by considering how CO_2 can affect the colloidal gold nanoparticles and its atmospheres. When colloidal gold solutions were bubbled with CO_2 gas, the surface as well as the surrounding medium of nanoparticles might be influenced by the CO_2 gas molecules which could induced a change in optical characteristics.

In fact, the CO_2 gas can change the pH of the solutions and the electrostatic repulsion among the nanoparticles (Mohammed 2013) as it bubbled through the colloidal gold nanoparticles solutions. Similarly the CO_2 gas can also affect surface of the nanoparticles by the adsorption of CO_2 molecules on colloidal gold and this adsorption could be from gas-phase adsorption or dissolved state adsorption. There could be different adsorption sites on the surface of metallic nanoparticles for example sites where molecules are physisorbed (or weakly adsorbed) are known as `normal' or N-sites while the sites on which the molecules interact strongly with the surface (chemisorbed) are called `extra' or E-sites. These E-sites are in fact various types of atomic-scale roughness sites (Akemann 1992).

The Possible factors which caused the change in the transmission spectra were adsorbed CO_2 molecules on N-sites of gold nanoparticles from the dissolved state in the colloidal solution(Kneipp 1995) and/or the change in the pH and the electrostatic repulsions. Perhaps the accumulative effect has induced a change in the electron charge density on the surface which caused a decrease in the transmission spectra of gold nanoparticles in the present of CO_2-flow.

Moreover a size dependent response in this phenomenon was also noticed. By increasing the size of the particle this declining trend in the transmission spectra further increased. It indicates that smaller size particles show highest sensitivity for gas which is in agreement with already reported results (Sadek 2010). This can be attributed by considering more adsorbing sites to accommodate additional CO_2 molecules and thus enhancing the interaction of incident light with surfaces resulting further decrease in transmission as represented in figure 3 (d).

4. CONCLUSIONS

Size dependent opticalgas sensing performance of citrate stabilized gold nanoparticles for CO_2 gas is studied in detail. A decrease in transmission spectra of colloidal solutionin the presence of CO_2-gas flow was recorded which was consider due to the possible effect of CO_2 molecules on the surfaces of nanoparticles.it was also found that smaller particles are more efficient for gas sensing as compared to the larger ones as largest change is transmission was recorded for smallest size nanoparticles.

REFERENCES

Liu, X., Cheng, S., Liu, H., Hu, S., Zhang, D., and Ning, H. (2012), "A Survey on Gas Sensing Technology," *Sensors,* **12,** 9635-9665.

Hodgkinson, J. and Tatam, R.P. (2013) "Optical gas sensing: a review", *Meas. Sci. Technol*.**24**, 012004 (59pp)

Dobrokhotov, V., McIlroy, D. N., Norton, M. G., Abuzir, A., Yeh, W. J., Stevenson, I., Pouy, R., Bochenek, J., Cartwright, M., Wang, L., Dawson, J., Beaux, M. and Berven, C. (2006), "Principles and mechanisms of gas sensing by GaN nanowires functionalized with gold nanoparticles"*J. Appl. Phys.***99**, 104302-104309

Saha, K., Agasti, S.S., Kim, C., Li, X., Rotello, V.M. (2012), "Gold Nanoparticles in Chemical and Biological Sensing"*Chemical Reviews*, **112**, 2739.

Dario, D., Lauren, P., Valentina, B., Giovanni, M., Michael, P., Paul, M., Alessandro, M. (2009)," Self-assembled gold nanoparticle monolayers in sol-gel matrices: synthesis and gas sensing applications", *Journal of Materials Chemistry*, **19**, 2051-2057

Sadek, A. Z., Moafi, A., Lau, D. M., McCulloch, D. G., Zheng, C., Hu, Z., Wlodarski, W., Kalantar-zadeh, K. (2010), "Highly dispersed gold nanoparticles on nitrogen doped carbon nanotubes for hydrogen sensing", *IEEE Sensors*, 386-390.

Young, S-J., Lin, Z-D, Hsiao, C-H.and Huang, C-S. (2012), "Ethanol gas sensors composed of carbon nanotubes with adsorbed gold nanoparticles", *Int. J. Electrochem. Sci.,***7**, 11634 – 11640.

Manera, M.G., Spadavecchia, J., Buso, D., de JuliánFernández, C., Mattei, G.,Martucci, A., Mulvaney, P., Pérez-Juste, J., Rella, R.,Vasanelli, L. andMazzoldi , P. (2008), "Optical gas sensing of TiO_2 and TiO_2/Au nanocomposite thin films" *Sensors and Actuators* B **132**, 107-115.

Kawaguchi, T., Shankaran, D.R., Kim, S.K., Matsumoto, K., Toko, K. and Miura, N. (2008), "Surface plasmon resonance immunosensor using Au nanoparticles for detection of TNT" *Sensors and Actuators* B **133**, 467-472.

Ganachari, S. V., Deshpande, R., Bhat, R., Rao, N.V.S., Huh, D.S. and Venkataraman, A. (2011), "Gas sensing characteristic of biofunctionalized gold nanoparticles", Journal of Bionanoscience, **5,** 107-112.

Zhang, H-L., Evans, S.D., Henderson, J.R., Miles, R.E. andShen, T-H.(2002), "Vapour sensing using surfacefunctionalized gold nanoparticles", Nanotechnology, **13**, 439-444.

Ma, Y. and Yung, L-Y. (2014), "Detection of dissolved CO_2 based on aggregation of gold nanoparticles" *Analytical Chemistry,* **86,** 2429-2435.

Raza, M.A., Kooij, E.S., van Silfhout, A., Zandvliet, H.J.W. and Poelsema, B. (2011), "Novel, highly selective gold nanoparticle patterning on surfaces using pure water" Journal of Colloid and Interface Science **364**, 304-310.

Brown,K.R., Walter, D.G. and Natan, M.J. (2000), "Seeding of Colloidal Au Nanoparticle Solutions. 2.Improved Control of Particle Size and Shape" Chem. Mater. **12**, 306-313

Siraj,K., Javaid, K., Pedarnig, J. D., Bodea, M. A.. and Naseem, S. (2013),"Electron beam induced nanostructures and band gap tuning of ZnO thin films" *J. Alloys. Compd.***563**, 280-284

S.Riaz, S.Naseem, S. (2009),"Effect of varing oxygen partial pressure on the properties of reactively evaporated zinc aluminuate thin films" *INT J MATER RES***100**(2), 234-237

Saeed,A.M., Riaz,R., Noor, R., and Naseem, S.(2013),." Structural and Optical Properties of Sol–Gel Derived $Zn_{1-x}Mn_xO$ Thin Films**"***Advanced Science Letters* 19(3), **78-794**

Saeed,A.M., Riaz,R., Noor, R., and Naseem, S.(2013),. Optical and Structural Properties of ZnO Thin Films for Solar Cell Applications**"** *Advanced Science Letters* **19**(3), 834-838 (2013)

Link, S., and. El-Sayed, M.A (2000), "Shape and size dependence of radiative, non-radiative and photothermal properties of gold nanocrystals," *Int*. *Rev*. *Phys*. *Chem*. ***19***, *409-453*.

Eustisa, S and El-Sayed, M.A. (2006), "Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes" *Chem. Soc. Rev.*, **35,** 209-217

Mohammad, F.S., Cole, S.R. and Kitchens, C.L (2013), "Synthesis and enhanced colloidal stability of cationic gold nanoparticles using polyethyleneimine and carbon dioxide" *ACS Sustainable Chem.Eng*.**1**, 826-832.

Akemann.W. and OTTO, A.(1992). "Roughness induced reactions of $N_2$and CO_2on noble and alkali metals" *Surf. Sci. **272**(1–3), 211–219*.

Kneipp, K., Wang, Y., Berger, A. J., Dasari, R. R. and Feld, M. S. (1995), "Surface-enhanced Raman scattering of CO_2 dissolved in aqueous colloidal solutions of silver and gold". *J. Raman Spectrosc*., **26**: 959–962.