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Growth of silver nanoparticles on silica matrix: Study by x-ray photoelectron spectroscopy, x-ray diffraction and TEM

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ABSTRACT

X-ray diffraction and X-ray photoelectron spectroscopy analyses are performed to investigate silver nanoparticles embedded in an amorphous SiO_2 matrix. The different silver contents and reaction temperatures were investigated. silver-silica nanocomposites are prepared by sol-gel method. After the drying, the sol-gel samples are annealed in air environment. Crystalline silver nanoparticles are identified in sol-gel samples (20–50 nm size). © 2013 Trade Science Inc. - INDIA

KEYWORDS

Ag nanoparticles;
Silica gel;
Solgel and temperature.

INTRODUCTION

Silver Nanoparticles are very promising materials because of potential applications in infrared optics, reversible optical recording, memory switching, inorganic photo resists, optical transmission media, humidity sensors, antireflection coatings, and that is why their investigation is of great interest^[1-6]. Metal nanoparticles embedded in an amorphous SiO_2 matrix are thoroughly investigated due to the quantum confinement effects and to the possible applications in electronics, optoelectronics and photo voltaics^[7-9]. The structure of silver nanoparticles in a SiO_2 matrix looks different, depending on the preparation method. Among various methods, the sol-gel technique^[7] is a promising low-temperature route that provides good homogeneity for the preparation of metallic nano-particles in thin coatings in a thermally stable dielectric solid oxide matrix such as SiO_2 . This process matches the demands of industries in terms of bulk preparation of materials with high den-

sity, high mechanical strength and high shock resistance, high specific area, compositional purity and optical grade quality. Nowadays, the sol-gel chemistry provides a means for preparing mixed oxides in which the mixing of two or more metal oxide phases can be controlled on both the molecular and the nanoscale. The different reactivity of individual components has been the major problem of the synthesis of mixed oxides, especially in the alkoxides based sol-gel process. The problem can be minimized by controlled pre hydrolysis of the less reactive precursor, by chemical modification of the precursors, by using single-source hetero bimetallic alkoxide precursors or by a non-hydrolytic sol-gel route^[7-12]. The microstructure is investigated by transmission electron microscopy (TEM). For amorphous silver nanoparticles, their interface with the SiO_2 matrix is not well-defined, as shown by many observations, including TEM^[13-19]. An open question that remains is the ionization state of silver inside these nanoparticles. It is expected that a charge transfer will occur between the

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silver atoms from the nanoparticles surface and the host matrix. This is a typical problem to be investigated by X-ray photoelectron spectroscopy (XPS)^[20-21]. A possible solution to circumvent this constraint is the XPS, i.e. by using an excitation line of higher energy. This way is chosen in the present work.

This paper focuses on the structural investigations of silver nanoparticles embedded in an amorphous SiO₂ matrix by XRD, XPS and TEM methods. The samples are investigated, prepared by sol-gel methods. In the sol-gel samples, amorphous silver nanoparticles are observed, with diameters depending on the silver concentration.

The stem of this study is in the results of our earlier report^[22], in which, we demonstrated the effect of temperature and time on Nd₂O₃-SiO₂ nanocomposites. The annealing temperature and time dependence of the formation of Nd₂O₃ nanocrystallites as well as their distribution in fused silica matrix were observed. We found that the average size of the silver nanocrystallites in a silica matrix was ~25 nm. The X-ray diffraction (XRD), (XPS) techniques and TEM data for silver silicates are presented.

EXPERIMENTAL

The principle and basic technique of the solgel process were described in detail in Reference^[22]. Silver silicates were prepared by mixing high purity reagents (CH₃CH₂O)Si (TEOS) Tetraethoxy silane (Aldrich 99.999), ethanol (Aldrich 99.9995), and deionized water. To prepare the samples different amount of silver was introduced in the pre-hydrolyzed solution in the form of nitrate under heating. The resultant homogeneous solutions were filled in a mold and placed in drying oven at room temperatures. The gelation occurred after some days. The crystallographic interpretations were performed by X-ray Diffractometer (D-8 advanced X-ray diffraction of M/s Bruker made) using Cu-K α wavelength ($\lambda=1.54059 \text{ \AA}$). XPS spectra were collected on Perkin-Elmer (model 1287) system, with a spectrometer using Al K α X-ray source (energy 1486.6eV) with pass energy 100meV for general scan and 40eV for core level spectra of each element. The particle size and aggregation state of particles were further measured with transmission electron micrograph (TEM, Jeol, JEM-1010, Japan) at 80 kV accelerating voltage.

RESULTS

X-ray photo electron spectroscopy (XPS)

Figures 1-5 shows XPS spectra recorded for all the catalysts respectively. In the present study the XPS was carried out in only three samples SiO₂, 0.5 wt % Ag-SiO₂ and 5 wt % Ag-SiO₂. From the Figure 1 we can see that the values of binding energy at 458 eV and lines at 464.03 eV for SiO₂, which indicates the presence of Si. The binding energy of the 0.5 wt % Ag-SiO₂ sample and that of 5 wt % Ag-SiO₂ is increased as compared to that of SiO₂. This is because the Fermi level, so that the conduction band electrons of SiO₂ may transfer to the Ag deposited on the surface of SiO₂, which results in a decrease in the outer electron cloud density of Si ions.

From the Figure 2 we can see that four O1s peaks appear after deconvolution, which can be attributed to lattice oxygen (529.34 eV), surface bridging oxygen (530.09 eV), surface hydroxyl oxygen (531.92 eV) and adsorbed oxygen (533.82 eV) in SiO₂.

With silver doping, we can see in Figure 3 and Figure 4 that the contribution of oxygen is same but an addition peak at 530.83 eV appears indicating the interaction of Ag-O.

This interaction is more prominent at higher Ag doping of 5 wt % in Figure 4. Also we can see that with this increased Ag-O interaction, the contribution from lattice oxygen decreased whereas that of surface hydroxyl

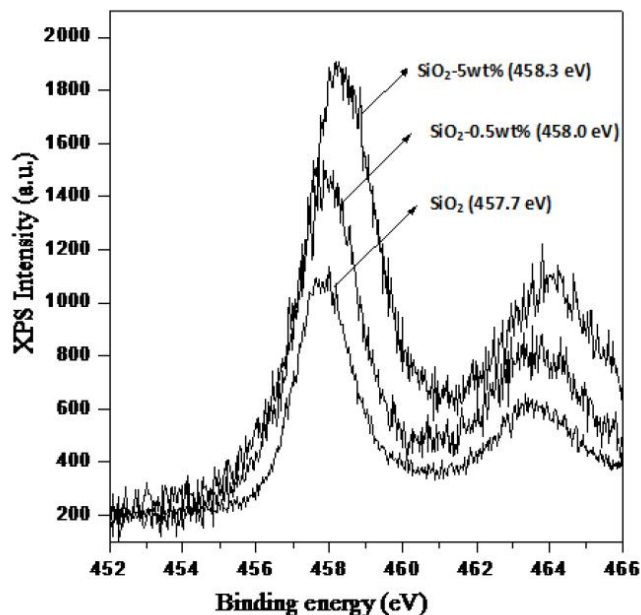
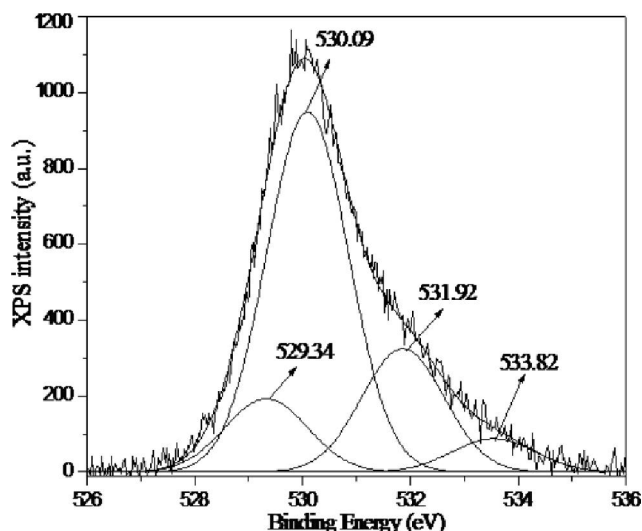
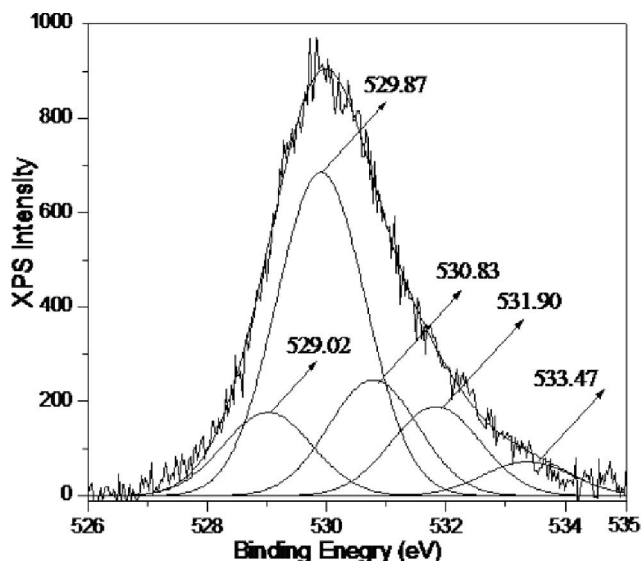


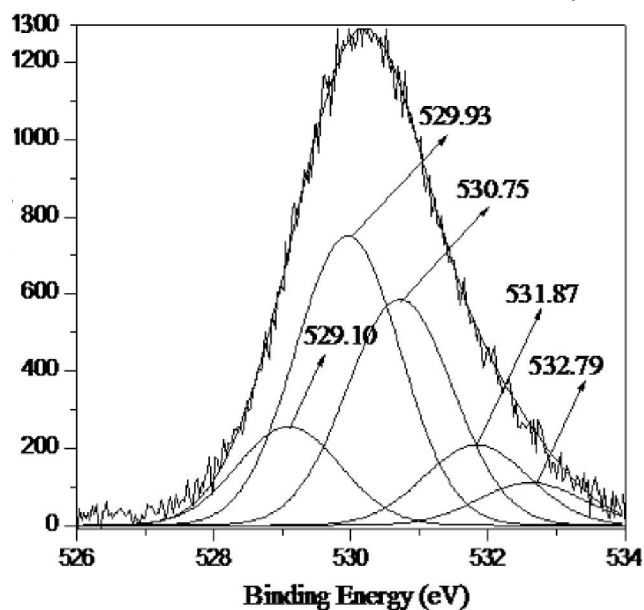
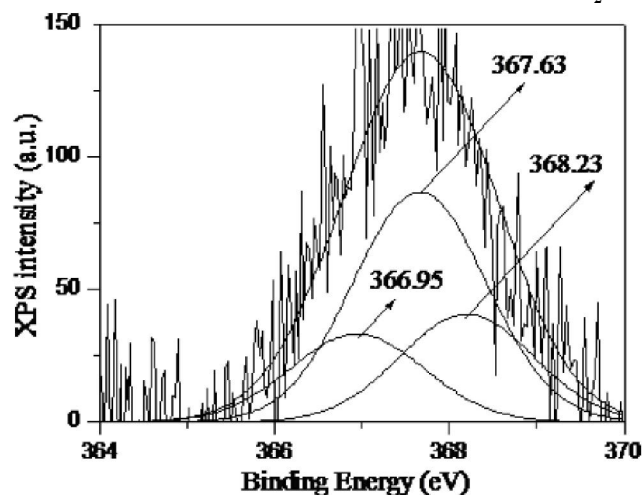
Figure 1 : XPS spectra of SiO₂, 0.5wt% Ag-SiO₂ and 5 wt% Ag-SiO₂

Figure 2 : XPS spectra of O1s of SiO₂Figure 3 : XPS spectra of O1s of 0.5 wt % Ag-SiO₂

increases, which is attributed to the deposited Ag enhancing the ability to adsorb O₂.

Figure 5 depicts the XPS core level spectra of Ag for the 5 wt % Ag doped SiO₂. The XPS spectra of Ag indicate that there are three components after deconvolution, attributed to AgO (366.95 eV), Ag₂O (367.63 eV), and Ag (368.23 eV), respectively^[7]. It must be noted that for silica samples doped with a very small doping of 0.5 wt% silver, the intensity of the Ag peak is close to the noise level, probably due to the detection limit of the XPS instrument.

As a result, we could not get core level spectra of Ag of 0.5 wt % Ag-SiO₂. At high concentrations, Ag ions and Ag coexist on the surface, but the amount of Ag species on the surface is increased remarkably.

Figure 4 : XPS spectra of O1s of 5 wt % Ag -SiO₂Figure 5 : XPS spectra of 5wt % Ag-SiO₂

X-ray diffraction (XRD)

Figure 6 shows the powder X-ray diffraction patterns for as-synthesized samples. The 'd' values and intensities of observed diffraction peaks match with the single crystalline silver form of the silver (JCPDS Card). X-ray diffraction pattern of as-synthesized particles shows broad peaks indicating ultra fine nature and small crystallite size of the particles. On annealing the samples at 400°C the X-ray diffraction patterns show an improvement in the sharpness and intensity of the peaks. The lattice parameters were calculated for all the compositions. It is observed that for as-synthesized samples, lattice parameters decreases from 8.4271 Å to 8.4093 Å with increase in silver content.

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The crystallite size of each composition was then determined by the Scherer relation:

$$D = 0.89 \lambda / b \cos q \quad (1)$$

where, λ is wavelength of X-ray, b is full width at half maximum (FWHM) measured in radians and q is the Bragg angle. On annealing, the crystallite size increases gradually and is attributed to the grain growth of the particles in the nano region at the temperatures well below the melting temperature of the bulk silver silicate.

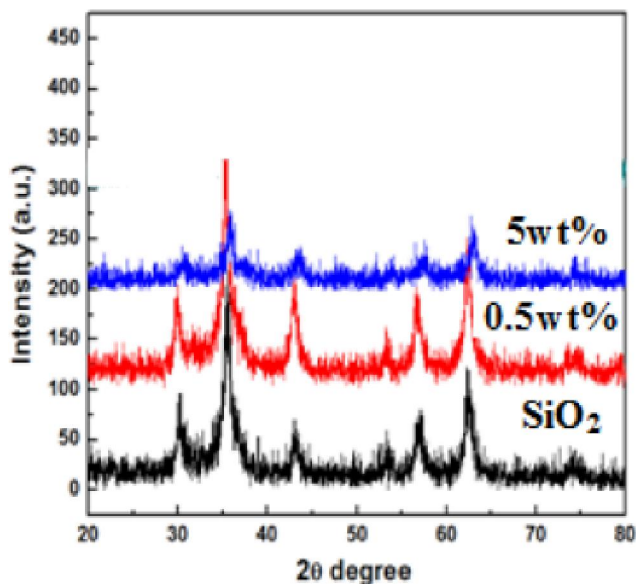


Figure 6 : X-Ray Diffraction (XRD) of (a) SiO₂ (b) 0.5wt% Ag doped SiO₂ (c) 5wt% Ag doped SiO₂

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) has provided further insight into the morphologies and structure detail of these silver-silica samples. Figure 7 shows

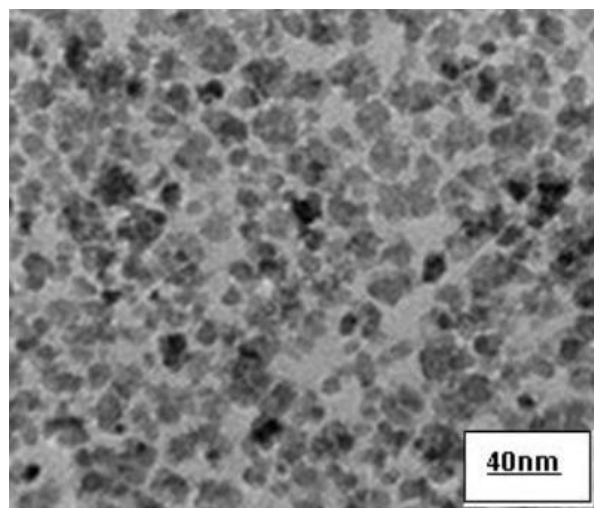


Figure 7 (a)

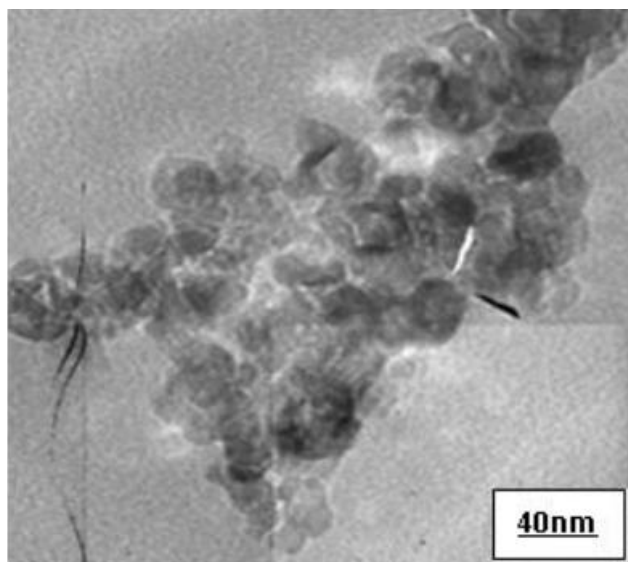


Figure 7 (b)

the TEM image of silver-silica samples. The observed size of silver nanoparticles by TEM micrograph is consistent with the size calculated by Debye–Scherrer formula. The peak of XRD patterns were considered for crystallite size study. The particle size increases with the increase in metal ion concentration.

CONCLUSION

Results obtained from XRD and various supporting techniques evidenced that silver is present in the lattice. Also XPS evidenced that both water and hydroxide are present in crystals. XRD combined with XPS, and TEM gives a good research suite for humidity sensing applications, a naturally grown composite material, characterization. Further investigation of potential of Transition Metals and reaction mechanism for substitution reaction are needed due to complex nature of inorganic and organic and inorganic/organic interfaces present in the structure.

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