Metal nanoparticle doped coloured coatings on glasses and plastics through tuning of surface plasmon band position

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Abstract. Several noble metal nanoparticles doped sol-gel derived thin coloured films have been synthesized and characterized. These are pure (Ag, Au, Cu and Pt), mixed/alloy (Ag–Cu, Au–Cu, Au–Ag and Au–Pt) nanoparticles in SiO₂, Au in mixed SiO₂–TiO₂ and SiO₂–ZrO₂, Au and Ag nanoparticles in inorganic–organic hybrid film matrices etc. This investigation leads to the development of tailor-made coloured coatings by tuning the surface plasmon resonance (SPR) band positions originating from the embedded nanometals by controlling mainly (i) refractive index of the film matrices and (ii) nanoalloy composition. In the later case a new layer-by-layer (two-layer) synthetic protocol has been developed to prepare binary nanoalloy particles with controlled atomic ratios.

Keywords. Metal (single/mixed/alloy) nanoparticles; surface plasmon; coloured coatings on glasses and plastics; layer-by-layer coatings by sol-gel; refractive index tuning; NLO material.

1. Introduction

Noble metal nanoparticles (mainly Au, Ag and Cu) have been studied extensively because of their unique linear (Sun and Xia 2003; Medda *et al* 2005a; Pal and De 2005; Jain *et al* 2006; Liz-Marzán 2006) and nonlinear optical properties (De *et al* 1996; Kiran *et al* 2004; Venkatram *et al* 2006). These unique properties are associated with their strong surface plasmon resonance (SPR), which are due to $d-d$ transitions pushed into the visible part of the spectrum. As a consequence they show very intense colouration and their optical properties depend strongly upon the particle size and shape, concentration, refractive index of the surrounding medium (embedding matrix), interparticle interactions, coupling and mixing of plasmon bands due to alloying of different metal nanoparticles etc (see, for example, Liz-Marzán 2006). Using these metal nanoparticles as a colouring source we have undertaken a research programme to develop several colour coatings applicable to glass and plastic substrates (Medda *et al* 2005a, b; Pal and De 2005; De and De 2006a; Pal and De 2007a). The manufacturing process involves preparation of sols using suitable metal organic precursors (e.g. alkoxides or functionalized alkoxides also known as inorganic–organic hybrid precursors) and soluble single or mixture of noble metal salts. The sols after controlled hydrolysis-condensation reactions could be applied to glass or plastic substrates by usual dip- or spin-coating technique. The as-prepared coatings are first dried and then heat-treated at 450°C and above (in case of glass) in di-

fferent gas atmospheres or cured photochemically through UV light (in case of plastic substrates). The heat treatment causes densification of the matrix as well as reduction of metal salts to the corresponding metal nanoparticles. On the other hand, UV curing causes polymerization of organic functionalities and inorganic networks, and reduction of metal salts simultaneously. In this programme, the SPR absorption in the visible spectrum of light (which causes intense colouration) arising from the embedded nanometals was tuned by controlling the following: (i) refractive index of the coating matrix, (ii) nanoalloy type and atomic ratio (pre-determined) and (iii) composition of nanoalloys formed by interlayer diffusion using a new two-layer (TL) approach (Pal and De 2005, 2007). In case of (i), we tried to keep the shape and size of nanoparticles similar in coating matrices having different refractive index values. The refractive indices are controlled by changing the ratios of two dielectrics (e.g. SiO₂ and TiO₂ or ZrO₂). In case of (ii) and (iii), so far SiO₂ has been used as the matrix. The different noble metal soluble salts (e.g. gold and copper chloride, silver and copper nitrate, gold and platinum chloride) in fixed ratios (pre-determined) are mixed with matrix-precursors to obtain the desired alloy/mixed nanoparticles. In case of (iii), a layer-by-layer (two-layer) deposition technique was employed to obtain tunable alloy nanoparticles. Here two successive overlapping individual layers containing different metal ion doped sols, respectively are deposited on glass substrates. These two-layer (TL) film assemblies when treated thermally/photochemically, interlayer diffusion of nanometal(s) causes alloying in a controlled way. The concept lying behind this new approach is described below. The synthesis of different binary alloys (e.g. Au–Cu (De *et al*

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2000; De and Rao 2003), Co–Ni (Mattei *et al* 2002) and Au–Pt (De and Rao 2005)) and mixed (e. g. Ag–Cu (De 1998)) nanoparticle doped coatings from sols obtained by simply mixing soluble nitrate or chloride salts into TEOS-derived silica sols followed by thermal annealing could be achieved using method (ii). However, this simple approach failed in the case of systems like Au–Ag because of non availability of Au- and Ag-salts remaining soluble in a common solvent. Thus in case of Au–Ag, a new TL protocol has been designed (Pal and De 2005). This approach works extremely well in obtaining films containing uniform Au–Ag nanoalloys with controlled atomic ratios. This new approach also works in other cases (e.g. Au–Cu (Pal and De 2007b)) where soluble salts are available.

In this article, our work related to the development of coloured coatings on glass and plastic substrates will be reviewed and presented in brief. Apart from the linear optical properties (colour), the nonlinear optical (NLO) properties are also of great interest for application of metal nanoparticle doped coatings in ultra fast optical switches. Some results will be highlighted at the end as references (Kiran *et al* 2004; Venkatram *et al* 2006).

2. Experimental

The individual metal (Au, Cu, Ag and Pt) nanoparticle doped coatings were prepared from SiO_2 and SiO_2 – TiO_2 hybrid sols using silicon, titanium, zirconium and substituted (functionalized) silicon alkoxides, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2$, AgNO_3 , H_2PtCl_6 , acetylacetone (*acac*), *n*-propanol, *n*-butanol, *i*-butanol and acidulated water. In case of mixed (binary) metal nanoparticles doped sols two soluble metal salts are incorporated into the sols in suitable proportions for desired alloy compositions. Coatings could be prepared either by the sol–gel dip- or spin-coating techniques followed by thermal annealing and/or UV curing. To control the matrix refractive index of SiO_2 : TiO_2 and SiO_2 : ZrO_2 molar ratios (nominal) were varied from 1:0 to about 1:4. In case of SiO_2 – TiO_2 system the oven dried (90°C) films were directly heated to 500°C in air to obtain the final dense films, whereas for SiO_2 – ZrO_2 system after oven drying a UV curing step was given before proceeding to further heat-treatment. The molar ratio of the metal to equivalent oxide ($\text{SiO}_2/\text{SiO}_2$ – $\text{TiO}_2/\text{SiO}_2$ – ZrO_2) was kept close to 3 equivalent mol% metal–97% oxide. In cases of inorganic–organic composite coatings applicable for plastic substrates, about 2.2–3.2 equivalent mol% metal was incorporated into the hybrid matrix (SiO_2 –polyethylene oxide (PEO)/ SiO_2 –PEO– TiO_2). Coatings were deposited on clean soda-lime silica, silica glass and polycarbonate substrates by dip-coating employing a lifting speed of 2–4 inches/min. The resulting films deposited on glass substrates were dried at 60°C for 60 min followed by annealing at 450°C for 30 min in air for the decompo-

sition of organics. Subsequent heat-treatments in controlled atmospheres were then followed. The maximum annealing temperature and gas atmospheres were varied in different systems. In case of two-layer coatings, the second layer has been deposited onto the first layer after drying at 60°C. The TL coating assembly was finally dried at 60°C for 30 min and subjected to UV and necessary thermal treatments. The coatings deposited on PC were first dried at 90°C followed by UV curing using a conveyerized UV curing machine. The coating thickness, estimated by a profilometer, was in the 200–1000 nm range. Undoped coatings were also prepared for the measurement of matrix refractive index values. The details of characterization techniques employed (e.g. measurements of coatings, thickness, refractive index, FTIR, UV-visible, XRD, TEM, energy dispersive X-ray analysis etc) in these studies were described elsewhere (Pal and De 2005; Medda *et al* 2005a).

3. Results and discussion

3.1 Refractive index controlled plasmon tuning

The SPR absorption position of nanometals was tailored by controlling the refractive index of the embedding matrix (Medda *et al* 2005a; De and De 2006b; De *et al* 2008). The optical absorption of metal nanoparticles is dependent mainly on concentration, size, shape and the nature of the surrounding medium. Among these the concentration is related to the intensity of absorption peaks. Therefore, if the concentration, size and shape of the nanoparticles can be kept similar then the influence of surrounding medium could be realized. In fact, the influence of the non absorbing surrounding medium (here coating matrix) is usually related to its refractive index (Mulaney 1996; Liz-Marzán 2006), since Mie theory predicts resonance to occur when $\epsilon_1(\omega) = -2\epsilon_m$, where $\epsilon_1(\omega)$ and ϵ_m are the real components of the metal dielectric function at angular frequency, ω and medium dielectric constant, respectively. Therefore, if the size- and shape effects of the nanoparticles are not considered, the position of SPR arising from the metal nanoparticles can be tailored by changing the refractive index of the embedding matrices. Using this idea, different coloured coatings on ordinary sheet glasses were prepared by incorporating Au nanoparticles in SiO_2 – TiO_2 and SiO_2 – ZrO_2 matrices having different refractive index values ranging from about 1.41–1.94. As for example the Au–SPR can be tuned from 540 nm to ~600 nm on going from SiO_2 to SiO_2 – TiO_2 (1:3) matrix, and as a consequence, different coloured coatings (pink, magenta, violet, royal-blue and blue) were obtained (Medda *et al* 2005a). Similar effects are also observed in case of Au in SiO_2 – ZrO_2 system (De *et al* 2008). In this case also the red-shifting of Au–SPR from 545–592 nm is clearly observed on going from SiO_2 : $\text{ZrO}_2 = 1:0$ to 1:4 due to the

Table 1. Au–SPR peak positions with respect to the refractive index of the embedding SiO_2 : TiO_2 film matrix (part of data presented in this table has been reproduced from Medda *et al* 2005a).

	Molar ratio (nominal) of SiO_2 : TiO_2	Annealing condition	Refractive index* (500°C)	Au–SPR position (nm) (500°C)
SiO_2 – TiO_2 series	1:0	90°C/500°C	1.411	542
	1:0.43	Do	1.604	555
	1:1	Do	1.713	572
	1:1.5	Do	1.862	580
	1:2.33	Do	1.913	588
	1:3	Do	1.939	600

*Refractive index values were measured from the undoped films

Table 2. Au–SPR peak positions with respect to the refractive index of the embedding SiO_2 : ZrO_2 film matrix (part of data presented in this table has been reproduced from De *et al* 2008).

	Molar ratio (nominal) of SiO_2 : ZrO_2	Annealing condition	Refractive index* (500°C)	Au–SPR position (nm) (500°C)
SiO_2 – ZrO_2 series	1:0	90°C/UV/500°C	1.410	546
	1:1	Do	1.698	558
	1:1.5	Do	1.728	571
	1:2.33	Do	1.765	581
	1:4	Do	1.847	592

*Refractive index values were measured from the undoped films

Figure 1. TEM of Au nanoparticle doped films obtained after final heat-treatment at 500°C. Image and corresponding size distributions of Au nanometals embedded in matrices SiO_2 : ZrO_2 (1:4), marked as (a) and (b) and SiO_2 : TiO_2 (2:3), marked as (c) and (d).

systematic increase of refractive index of the matrices after heat-treatment at 500°C. Tables 1 and 2 show the

SPR absorption peak positions of the final heat-treated (500°C) coatings arising from the embedded Au nanoparticles in refractive index controlled SiO_2 – TiO_2 and SiO_2 – ZrO_2 film matrices, respectively. The corresponding refractive index values of the undoped films are also shown in tables 1 and 2. Clearly, the Au SPR is systematically red-shifted with increasing refractive index of coating matrices. It may be pointed out here that the coatings are transparent and spot-free and sufficiently hard for any kind of practical applications. Furthermore as the extinction coefficient of such SPR absorptions are very high, small amount of doping of such nanometals causes intense colouration.

To check the shape and size of the Au nanoparticles, TEM and XRD studies were undertaken. We found similar shape and size distributions of Au nanoparticles embedded in respective series of SiO_2 – TiO_2 and SiO_2 – ZrO_2 systems. In case of SiO_2 – TiO_2 series presence of spherical Au nanoparticles of an average diameter of 20 ± 3 nm has been observed whereas in the SiO_2 – ZrO_2 system Au nanoparticles having diameter of about 10 nm and a few bigger Au nanoplates of hexagonal and triangular shapes are found to co-exist. The generation of these Au nanoplates most probably originated from the UV-photo reduction of HAuCl_4 in the inorganic–organic hybrid matrix because earlier reports showed UV decomposition of HAuCl_4 favours generation of Au nanotriangles and hexagons in solution (Zhou *et al* 1999). The 10 nm particles which are present in >70% population are expected to dominate the optical features in case of Au/ SiO_2 – ZrO_2

films. As the shape and size distributions of Au nanoparticles are different we observed some anomalies in the SPR peak positions of the two series of final heat-treated film samples (tables 1 and 2). As for example the refractive index values of $\text{SiO}_2:\text{TiO}_2$ (1 : 1.5) and $\text{SiO}_2:\text{ZrO}_2$ (1 : 4) films are comparable, however, the Au-SPR positions are observed in different positions at 580 and 592 nm, respectively. This difference could be due to the presence of nanoplates (anisotropic) in the $\text{SiO}_2:\text{ZrO}_2$ films which usually pushed the SPR towards higher wavelengths. The XRD of $\text{Au}/\text{SiO}_2\text{-TiO}_2$ films showed weak broad peaks corresponding to *fcc* Au nanometals. On the other hand, $\text{Au}/\text{SiO}_2\text{-ZrO}_2$ films showed relatively strong peaks corresponding to the Au (111) and Au (222) reflections only. This observation supports the presence of 2D Au nano-

plates in $\text{Au}/\text{SiO}_2\text{-ZrO}_2$ films. The difference in size and shape of Au nanoparticles in the two series could be due to the UV treatment step given prior to heat-treatment in case of $\text{SiO}_2\text{-ZrO}_2$ system. In this series, the UV treatment step prior to thermal treatment was essential for the generation of Au nanoparticles and decomposition of *Zr-acac* linkages. These UV treated films when heat-treated at 500°C produced uniform and transparent coloured coatings on glass substrates. Figure 1 shows TEM of two representative final heat-treated $\text{Au}/\text{SiO}_2\text{-TiO}_2$ (2 : 3) and $\text{Au}/\text{SiO}_2\text{-ZrO}_2$ (1 : 4) samples along with the size distributions of embedded Au nanoparticles.

In another development, *in situ* generation of Ag nanoparticles in the refractive index controlled inorganic-organic hybrid host ($\text{SiO}_2\text{-TiO}_2\text{-PEO}$) leads to the formation of abrasion resistant coloured coatings (yellow to pink) on plastic substrates (Medda *et al* 2005b). In this case Ag nanoparticle incorporated inorganic-organic hybrid $\text{SiO}_2\text{-TiO}_2$ films were prepared from sols derived from tetraethyl orthosilicate, 3-(glycidoxypopyl)-trimethoxysilane, titanium isopropoxide and silver nitrate following a sol-gel dip-coating method. Hydrolysis-condensation of alkoxy groups and polymerization of epoxy groups formed the inorganic ($\text{SiO}_2/\text{TiO}_2$) and polyethylene oxide (PEO) network, respectively. These films were cured thermally ($\sim 100^\circ\text{C}$) and photochemically using a conveyorized UV curing machine. In this system by controlling the $\text{SiO}_2/\text{TiO}_2$ molar ratio the matrix refractive index can be tuned from 1.475 to 1.71. Accordingly, the Ag-SPR has been shifted from about 420 nm (refractive index, 1.475) to about 500 nm (refractive index, 1.71). As a result the colour of the film can be tuned to any colour arising from

Figure 2. Optical absorptions and the corresponding TEM images of Ag nanoparticle doped $\text{SiO}_2\text{-PEO}$ hybrid films after UV irradiations with energies 5.3 J/cm^2 (a) and (b); 31.8 J/cm^2 (c) and (d). (The curves shown in (a) and (c) are reproduced from De and De 2006a).

Figure 3. Schematic representation of the 2L protocol used for the generation of alloy nanoparticles in controlled atomic ratios inside the film matrices.

Figure 4. UV-visible spectra showing the SPR arising from Au-Ag (1 : 1) alloy nanoparticles obtained using the new 2L approach. The SPR of the corresponding Au- and Ag-nanoparticle doped single-layer films are also shown. The composition of the films is 3 equivalent mol% metal-97% SiO_2 and accordingly the films are marked as Au_3 , Au_3Ag_3 and Ag_3 in the body of the figure. (The curves shown in this figure are reproduced from Pal and De 2005).

absorptions in the range of 420–500 nm. TEM studies of this series show presence of very small Ag nanoparticles of size ranges 3–5 nm. The adhesion (5B as per ASTM D3359) and abrasion resistant (pencil hardness value, 3–4H as per ASTM D3363 standard) qualities of these hybrid films are very good and can, therefore, be applicable as scratch resistant coloured coatings on transparent polycarbonate substrates.

We have also noticed controlled coarsening phenomena of Ag nanoparticles in SiO_2 -PEO hybrid matrix by UV light of different energies (De and De 2006a). A single surface plasmon resonance (SPR) band due to Ag nanoparticles has been observed at 419 nm when the Ag nanoparticles doped SiO_2 -PEO film is cured at 90°C and UV-treated with energy, 5.3 J/cm² (figure 2a). The corresponding TEM image (figure 2b) shows presence of Ag nanoparticles of mainly 3–4 nm (90–95%) in size. A few (5–10%) bigger nanoparticles of size ranges 10–25 nm are also visible. The Ag-SPR band is gradually split and finally showed three peaks at 361 (shoulder), 391 and 461 nm upon increasing the UV treatment energy up to 31.8 J/cm² (figure 2c). In this case the TEM study shows (figure 2d) presence of larger Ag nanoparticles of different shapes (spheroidal, elongated and fractal type small aggregates). Therefore, the modification of optical spectra of Ag nanoparticles occurred due to the coarsening of small Ag nanoparticles to the large spheroidal, elongated and fractal type small aggregates after UV treatment. The splitting of Ag-SPR band is found to be consistent with the average aspect ratio (calculated from TEM image) of Ag nanometals of anisotropic shapes (De and De 2006a). Using this simple approach the coarsening of Ag nanoparticles could be controlled by controlling the UV treatment energies.

Tuning of Au SPR band has also been accomplished using the inorganic-organic hybrid film matrix like SiO_2 - TiO_2 -PEO (equivalent SiO_2 : TiO_2 = 2 : 3). In this case the refractive index of the hybrid matrix can be controlled with respect to the UV irradiation energies (De and De 2006b). As a consequence the Au-SPR has been red-shifted with increasing refractive index of the matrix. The study reveals tunable coloured coatings (pink to blue-violet) when applied on glass as well as plastic substrates.

3.2 Alloy composition controlled plasmon tuning

It has been observed that the compositions of alloy nanoparticles (Au/Cu and Au/Pt) in SiO_2 film matrix could be controlled by controlling simply the nominal molar ratios of metal salt precursors in the silica sol (De *et al* 2000; De and Rao 2003, 2005). This process of doping works well if the respective metal salts remain soluble in the solvent mixture used for the preparation of sols. However, the process failed completely when two metal salts did not remain soluble in the sols. As for example in

case of Au/Ag system the most commonly available and used precursors are HAuCl_4 and AgNO_3 . These salts are

Figure 5. (a) UV-visible spectra of the final heat-treated (750°C/ H_2 -Ar) 2L film containing $\text{Au}_{0.58}\text{Cu}_{0.42}$ nanoparticles and the Au- and Cu-nanoparticle doped single-layer films, (b) TEM image of $\text{Au}_{0.58}\text{Cu}_{0.42}$ nanoparticle doped TL films obtained after final heat-treatment at 750°C. Inset of (b) shows the high resolution image and (c) the corresponding XRD spectrum showing only $\text{Au}_{0.58}\text{Cu}_{0.42}$ (111) reflection. (Part of the curves shown in (a) are reproduced from Pal and De 2007b).

individually soluble in silica sol; however, when they are attempted to mix precipitation of AgCl resulted instantaneously. We, therefore, developed a new sol-gel 2-layer (2L) protocol (shown schematically in figure 3) for the preparation of Au-Ag alloy nanoparticles. This strategy involves deposition of two successive overlapping individual layers of Au- and Ag-doped sols, respectively on glass substrates followed by UV treatment and thermal annealing (Pal and De 2005). The alloy formation with tunable Au/Ag compositional control occurred in amorphous glassy matrix through interlayer diffusion of Ag and Au in the solid state. This new 2L synthetic process also works to prepare other bimetallic alloy nanoparticle (e.g. Au/Cu) doped coatings.

The above synthetic process has the following interesting observations: (i) the alloy nanoparticles are formed through interlayer diffusion controlled mechanism; (ii) the interlayer diffusion is again controlled by the thermal annealing temperature and time; so the formation of intermediate alloy compositions of nanoalloys could be arrested and the product can be isolated; (iii) the desired final nanoalloy particles could also be obtained by controlling the concentrations of individual metals in the respective layers using proper annealing conditions and (iv) the process is suitable for other binary systems. Using this new 2L approach we have synthesized several types of Au-Ag nanoalloy incorporated SiO_2 films by simply changing the concentration of metals in the individual layers. As, for example, if we intend to prepare Au-Ag (1 : 1) nanoalloy as a final composition then the individual layers should contain similar molar concentrations of Au and Ag, and this can be done by applying two successive overlapping coatings of equal thickness containing same equivalent amount (molar) of the two metals. Therefore, the individual coating sols have to be prepared carefully so that the equivalent metal/matrix (SiO_2) composition and other sol preparation parameters (nature and amount of solvents/hydrolysis-condensation reactions/room temperature/humidity etc.) remain identical. As an example the synthesis of Au-Ag (1 : 1) nanoalloy (final composition) incorporated films is described below (Pal and De 2005). First, Au-doped coating was deposited on cleaned substrate (here $M_1 = \text{Au}$ as shown in figure 3) and dried at 60°C for 30 min followed by a second coating applied using Ag-doped sol (here $M_2 = \text{Ag}$ as shown in figure 3) onto it. The concentrations of the Au and Ag in the respective layers and their individual coating thicknesses are kept similar. The 2L coating assembly was again dried at 60°C for 30 min followed by UV treatment. UV-visible spectral analysis of this UV treated film shows peaks at 421 and 542 nm corresponding to the Ag- and Au-SPR, respectively thus confirming the formation of Ag and Au nanoparticles in the individual layers. This 2L coating assembly was then heated cumulatively at 450, 500 and 550°C in air. The UV-visible spectrum of the respective heat-treated films showed one intense SPR peak in

between the Au- and Ag-SPR peak position at 504 ($450^\circ\text{C}/1\text{ h}$), 497 ($500^\circ\text{C}/1\text{ h}$), 480 ($550^\circ\text{C}/1\text{ h}$) and 468 nm ($550^\circ\text{C}/2\text{ h}$), respectively due to the formation of Au-Ag nanoalloys. The compositions of the intermediate and final nanoalloy are $\text{Au}_{4.3}\text{Ag}_1$, Au_3Ag_1 , $\text{Au}_{1.5}\text{Ag}_1$ and Au_1Ag_1 , respectively (Pal and De 2005). It may be mentioned here that the unalloyed Ag remains as an oxidized species (which is optically non-absorbing) in the intermediate heat-treated films. During heat-treatment, such oxidized silver as well as very small Au nanoparticles come into contact through interlayer diffusion and form alloy nanoparticles inside the silica films. If the concentrations of M_1 and M_2 (figure 3) is varied keeping the above final heat-treatment schedule (slight modification may be required on case to case basis), almost any desired Au-Ag nanoalloy incorporated films could be prepared using this approach (Pal and De 2007). Figure 4 shows optical absorption spectra of Au-Ag (1 : 1) alloy nanoparticle incorporated film prepared using the new 2L protocol. The spectra of individual single-layer Au- and Ag-nanoparticle doped films are also shown in figure 4.

This new 2L approach also works well in Au-Cu (1 : 1) system (Pal and De 2007). In this case heat-treatments were carried out in H_2 -Ar (reducing) atmosphere to reduce the Cu ions. Here also Au-Cu nanoalloy particles of variable atomic ratios were found to be generated as intermediates before the formation of desired final Au-Cu alloy nanoparticles. During such annealing conditions, Au-Cu nanoalloys of compositions $\text{Au}_{0.84}\text{Cu}_{0.16}$, $\text{Au}_{0.75}\text{Cu}_{0.25}$ and finally $\text{Au}_{0.58}\text{Cu}_{0.42}$ were formed after heat-treatments at 450, 600 and 750°C , respectively in H_2 -Ar atmosphere. As a result, the UV-visible and XRD analyses of the respective heat-treated films show the shifting of alloy SPR (in between Au- and Cu-SPR) and d -spacing in accordance with the alloy compositions. TEM and XRD analyses confirm the formation of highly $\langle 111 \rangle$ oriented growth of all intermediates and final Au-Cu nanoalloy particles inside the 2L film matrix. We, therefore, concluded that the alloy formation took place mainly through the diffusion and gradual dissolution of Cu atoms onto the $\langle 111 \rangle$ planes of Au and intermediate Au-Cu nanoalloy crystals. The optical spectra of final heat-treated 2L film containing $\text{Au}_{0.58}\text{Cu}_{0.42}$ alloy nanoparticles and single layer Au- and Cu-nanoparticle doped films are shown in figure 5a. The appearance of an intense alloy-SPR in between Au- and Cu-SPR indicates the formation of Au-Cu alloy. TEM study (figure 5b) of this film shows presence of $\langle 111 \rangle$ oriented $\text{Au}_{0.58}\text{Cu}_{0.42}$ nanoalloy particles. The high resolution image of one such nanoparticle is shown in the inset of figure 5b. The corresponding XRD of the film is presented in figure 5c. The appearance of reflections corresponding to only $\langle 111 \rangle$ crystalline plane confirms the oriented growth of the nanoalloy particles. The lattice d -spacing calculated from the XRD and also from high resolution image corresponds with the composition, $\text{Au}_{0.58}\text{Cu}_{0.42}$ (figures 5b and c).

Figure 6. Photographs of (a) Au nanoparticle doped $\text{SiO}_2\text{-TiO}_2$ films with refractive index control (see table 1). The $\text{SiO}_2 : \text{TiO}_2$ molar ratios are 1 : 0 (1), 1 : 0.43 (2), 1 : 1 (3), 1 : 1.5 (4) and 1 : 2.33 (5), (b) Au-Ag alloy nanoparticle doped films with controlled atomic ratios generated by TL strategy. The alloy compositions are: Au_1Ag_0 (1), $\text{Au}_{0.81}\text{Ag}_{0.19}$ (2), $\text{Au}_{0.6}\text{Ag}_{0.4}$ (3), $\text{Au}_{0.5}\text{Ag}_{0.5}$ (4) and Au_0Ag_1 (5) (Photos marked as 1–4 in (a) are reproduced from Medda *et al* 2005a).

The nonlinear optical (NLO) characterizations of some of our metal nanoparticle doped films were carried out to show their potential as NLO materials. The films deposited on glass substrates could withstand high intensity laser lights without any damage. The mixed Ag–Cu nanoparticle doped SiO_2 films (De 1998) showed self-defocusing nonlinearity and a good NLO absorption leading to the excellent optical limiting (OL) behaviour (Kiran *et al* 2003, 2004). Au nanoparticle doped $\text{SiO}_2\text{-TiO}_2$ films having refractive index controlled tunable Au–SPR (see §3.1a) exhibit good optical switching behaviour (Venkatram *et al* 2006). It has been observed that the refractive indices of the matrices around the Au–nanometals play an important role in modulating good photo switching.

4. Conclusions

In this paper we have shown tuning of SPR absorption positions of embedded nanometals inside dielectric matrices leading to the generation of several coloured coatings on glass and plastic substrates. The use of such intense colour generating chromophores in coating matrices can be utilized in a controlled fashion for technological applications. As, for example, photographs of two sets of coloured coatings are presented in figure 6. In the first set (figure 6a), same size and shaped Au nanoparticles (with similar concentrations) are embedded in dielectric coating

matrices ($\text{SiO}_2\text{-TiO}_2$) with different refractive index values (see §3.1), which causes systematic red-shifting of Au–SPR and in the second set (figure 6b) the colour of the film changes due to the presence of Au–Ag alloy nanoparticles of different atomic ratios (see §3.2), generated by the new TL protocol. Some of the above metal nanoparticle doped films showed good nonlinear optical (NLO) properties for application in optical limiting and switching.

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