Core–shell nanoparticles based on an oxide metal: ReO_3@Au (Ag) and ReO_3@SiO_2 (TiO_2)†

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Core–shell nanoparticles based on metallic ReO_3 nanoparticles have been prepared for the first time. The nanoparticles with the metallic shell *viz.* ReO_3@Au and ReO_3@Ag were prepared by the reduction of metal salts over ReO_3 nanoparticle seeds. ReO_3@SiO_2 and ReO_3@TiO_2 core–shell nanoparticles were prepared by the hydrolysis of the organometallic precursors over the ReO_3 nanoparticles. The core–shell nanoparticles have been characterized by transmission electron microscopy, optical absorption spectroscopy, energy dispersive X-ray spectroscopy, X-ray diffraction and Raman spectroscopy. The ReO_3@Au and ReO_3@Ag core–shell nanoparticles show composite plasmon absorption bands comprising contributions from both ReO_3 and Au (Ag) whereas ReO_3@SiO_2 and ReO_3@TiO_2 show shifts in the plasmon bands depending on the refractive index of the shell material.

Introduction

Core–shell nanoparticles constitute an important group of nanomaterials. Core–shell nanoparticles involving metallic nanoparticle cores and shells of oxides, semiconductors and other metals have been prepared and characterized. Similarly, core–shell particles with metal oxide cores and metallic oxide shells have also been synthesized and characterized. A variety of synthetic procedures have been employed for the synthesis of core–shell structures[1] which include precipitation,[2,3] micro-emulsion, reverse micelles,[4–6] sol–gel condensation,[7] layer-by-layer adsorption[8,9] and graft polymerization.[10] Among the various core–shell particles those containing cores of metals such as Au and Ag form a majority and there are a large number of papers in this area for example core–shell particles of the type Ag@Au,[11] Au@Ag[12,13] have been prepared and their properties reported. Similarly, core–shell particles of the kind Au@SiO_2,[14] Au@SnO_2,[15] Au@TiO_2[16–19] and Fe_3O_4@Au[20] have also been characterized by various techniques. Recently, nanoparticles of ReO_3 which is a good metal have been prepared and characterized.[21] Since ReO_3 is a metal which looks like copper and conducts like copper, we considered it important to investigate core–shell nanostructures formed with such an oxide metal as the core, with the noble metals and metal oxides as shell materials. It is noteworthy that ReO_3 gives rise to a plasmon band in the visible region just like gold and copper. Core–shell particles comprising such ReO_3 cores may indeed be useful as sensors and other applications. In this article, we describe the synthesis and properties of novel core–shell particles based on ReO_3 nanocrystals. The systems studied include ReO_3@Au, ReO_3@Ag, ReO_3@SiO_2 and ReO_3@TiO_2.

Experimental

The preparation of the ReO_3-based core–shell nanoparticles involved a two-stage synthetic methodology. The first step involved the synthesis of the ReO_3 nanoparticles following the procedure reported by us elsewhere[21] and the second involved the use of these nanoparticles as seeds in various reaction solutions containing the precursor for the shell-material and subsequently reducing (in the case of gold and silver) or hydrolyzing (in the case of TiO_2 and SiO_2) the shell-material over the ReO_3 nanoparticles.

The synthesis of ReO_3 nanoparticles involves the preparation of the rhenium(VII) oxide–dioxane complex, Re_2O_7–$(C_4H_8O_2)_x$ as the starting material (following the literature procedure[22,23]) and its solvothermal decomposition in toluene to yield the desired nanoparticles. In a typical synthesis, 0.025 g (0.12 mmol) of Re_2O_7 was taken in a 10 mL round-bottomed flask and 0.25 mL (2.93 mmol) of anhydrous 1,4-dioxane was added to it. This mixture was warmed in a water bath maintained at 70 °C and then frozen in an ice bath alternatively until rhenium(VII) oxide–dioxane complex (RDC) precipitated out as a dense, pearl gray deposit. The complex was dissolved in 2 ml (30.08 mmol) of ethanol and was taken in 45 mL of toluene and sealed in a Teflon-lined stainless steel autoclave of 80 mL capacity (at 70% filling fraction). It was then heated at 200 °C for 4 hours. The red ReO_3 nanoparticles (12 nm diameter) were washed several times with acetone. The particle size of ReO_3 could be increased by increasing the RDC concentration keeping the amount of toluene and the filling fraction of the autoclave constant. XRD patterns show the ReO_3 nanoparticles to be crystalline with a cubic structure (space group $Pm\bar{3}m$, a = 3.748 Å, JCPDS-00-24-1009).[21] The dried ReO_3 particles could be readily redispersed in ethanol or DMF.

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For the synthesis of ReO₃@Au core–shell particles, auric ions were reduced over ReO₃ seeds following a modification of the method of Enüstün and Turkevich.[24] A stock solution of 10^{-2} M HAuCl₄ in ethanol was prepared and used subsequently for the reactions. Although ethanol solutions themselves are quite stable, the HAuCl₄ "stock" solution in ethanol was prepared afresh for each series of reactions and was not stored to avoid any reduction. For the preparation of core–shell nanoparticles, the ReO₃ : Au molar ratio was kept at 1 : 2 and 1 : 4 and the amount of ReO₃ to be added to the reaction solution calculated accordingly *viz.* 3 mg and 1.5 mg of ReO₃ nanoparticles for the 1 : 2 and 1 : 4 reactions, respectively (keeping the HAuCl₄ concentration constant). In a typical synthesis, 100 ml of the HAuCl₄ stock solution containing the ReO₃ seeds was sonicated for 20 minutes (to disperse the ReO₃ nanoparticles). To the reaction mixture was then added 1.5 ml of 1% aqueous trisodium citrate solution dropwise with stirring. The solution was allowed to stir overnight. The nanoparticles so formed precipitated out of the solution and were collected aided by centrifugation. The nanoparticles were washed several times with ethanol.

For the synthesis of ReO₃@Ag core–shell particles, Ag⁺ ions were reduced over ReO₃ seeds by the procedure of Lee and Meisel.[25] A stock solution of 10^{-3} M AgNO₃ in water was prepared and used subsequently for the reactions. For the preparation of core–shell nanoparticles, the ReO₃: Ag molar ratio was kept at 1 : 2 and 1 : 3 and the amount of ReO₃ to be used in the reaction was kept constant at 5 mg per reaction whereas the volume of the AgNO₃ aqueous solution and the volume of the 1% trisodium citrate solution to be added was calculated accordingly. In a typical synthesis, 5 mg of ReO₃ was dispersed in 30 ml of ethanol aided by sonication for 20 minutes and then to this solution was added the calculated amount of AgNO₃ stock solution (43 ml for 1 : 2 particles and 86 ml for the 1 : 4 particles). To this was added 1% aqueous trisodium citrate solution (0.86 ml for 1 : 2 and 1.72 ml for 1 : 4) dropwise with stirring. The solution was allowed to stir overnight. The nanoparticles so formed precipitated out of the solution and were collected aided by centrifugation. The nanoparticles were washed several times with ethanol.

For the synthesis of ReO₃@SiO₂ core–shell particles, tetra-ethylorthosilicate (TEOS) was hydrolyzed over ReO₃ seeds by using the method reported by Stöber *et al.*[26] The amount of ReO₃ nanoparticles was kept constant at 5 mg per reaction while the amount of TEOS was varied accordingly so that the ReO₃ : SiO₂ molar ratio comes to 1 : 2, 1 : 3 and 1 : 4. A solution of ethanol : water : ammonium hydroxide = 98 : 31 : 4 was prepared and sonicated with ReO₃ nanoparticles for 20 minutes to obtain a uniform solution. To this was added the TEOS (in ethanol) dropwise with stirring. The solution was allowed to stir overnight. The solution assumed a faint yellow tinge (a change in colour from the dark green colour of ReO₃ dispersion) and the colour of the solution deepened with the increase in the silica content.

For the synthesis of ReO₃@TiO₂ core–shell particles, titanium tetra(*n*-butoxide) (TOB) was hydrolyzed over ReO₃ using a modification of the procedure reported by Scolan and Sanchez.[27] The amount of ReO₃ was kept constant at 5 mg per reaction whereas the amount of TOB was varied accordingly to keep the molar ratio of ReO₃ : TiO₂ at 1 : 2 and 1 : 4. Two solutions were prepared for a typical reaction: one containing 5 mg of ReO₃ and 0.8 M H₂O in dimethylformamide (DMF) and the other comprising of equimolar amounts of TOB and acetylacetone in ethanol in a concentration of 5.75 mM each. Both the solutions were sonicated for 20 minutes each to obtain clear mixtures and then the TOB containing solution was added to the ReO₃ solution dropwise with stirring while heating at 80 °C. After 90 minutes the colour of the solution changes from the dark green colour of ReO₃ to light yellow and this colour deepened with the increase of the titania content.

The core–shell nanoparticles were characterized by transmission electron microscopy (TEM), optical absorption spectroscopy, energy dispersive X-ray spectroscopy (EDAX), X-ray diffraction (XRD) and Raman spectroscopy. Core–shell nanoparticles were repeatedly prepared by the procedures described above to collect sufficient samples for characterization. For transmission electron microscopy, ethanol dispersions of the nanoparticles were taken on holey carbon-coated Cu grids, and the grids dried in air. The grids were examined using a JEOL (JEM3010) microscope operating with an accelerating voltage of 300 kV. Electronic absorption spectra were recorded using a Perkin-Elmer spectrometer. Powder X-ray diffraction patterns for the nanoparticles were obtained using a Philips X'Pert diffractometer employing the Bragg–Brentano configuration. The EDAX spectra were recorded using a LEICA S440i SEM. Raman spectra for the metal oxide coated particles were recorded using LabRAM HR800 using 632 nm laser as the excitation source.

Results and discussion

We prepared ReO₃ nanoparticles in the diameter range of 8.5–32.5 nm by the decomposition of the Re₂O₇–dioxane complex under solvothermal conditions. In Fig. 1(a), we show a TEM image of the ReO₃ nanoparticles with an average diameter of 12 nm. The size distribution histogram (shown as upper inset in Fig. 1(a)) shows that the particles are reasonably monodisperse with the diameters varying between 10 nm and 14 nm. The lower inset in Fig. 1(a) shows a high-resolution electron microscope image of an 8.5 nm particle. The 8.5 nm particle shown here was obtained from a separate preparation and does not correspond to the TEM images of Fig. 1(a). The lattice spacing of 3.77 Å corresponds to the (100) interplanar distance in the ReO₃ crystals. ReO₃ is known to exhibit a plasmon absorption band in the visible region just like gold and copper.[28] It is well known that the surface plasmon resonance is the coherent excitation of the free electrons within the conduction band, leading to an in-phase oscillation.[29] The surface obviously plays an important role for the polarizability of the metal and therefore shifts the resonance to optical frequencies. In Fig. 1(b), we show the electronic absorption spectra of the ReO₃ nanoparticles prepared by us. It is evident from the spectra that the λ_{max} of the absorption band shifts to the lower wavelengths with the decrease in the particle size. The λ_{max} values for the 32.5, 12 and 8.5 nm nanocrystals are 543, 507 and 488 nm respectively. Such a blue-shift of the surface plasmon band with decreasing particle size occurs in

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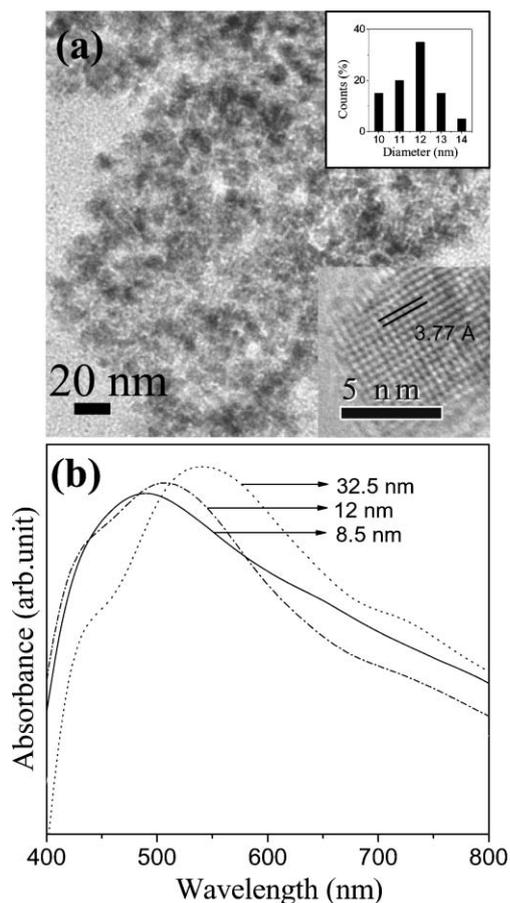
Fig. 1 (a) TEM image of ReO_3 nanocrystals with an average diameter of 12 nm. Upper inset shows the size distribution histogram and the lower one shows the single particle HREM image of the 8.5 nm particle, (b) UV-visible spectra of ReO_3 nanocrystals with average diameters of 8.5, 12 and 32.5 nm.

gold nanoparticles as well.[30] The surface of ReO_3 nanoparticles could readily adsorb organic molecules such as pyridine, pyrazine and pyrimidine. Evidence for bonding between the surface of the ReO_3 nanoparticles and the adsorbed molecules has been found by surface enhanced Raman scattering effect of pyridine, pyrazine and pyrimidine on the surfaces of ReO_3 nanoparticles. Thus, Raman bands of all these aza-aromatics adsorbed on ReO_3 surface show red-shift and large intensification compared to pure analyte Raman band.[31]

The various core–shell nanoparticles prepared by us were characterized by TEM. In Figs. 2(a) and (b), we show typical low-magnification TEM images in the case of ReO_3@Ag and ReO_3@SiO_2 core–shell nanoparticles. The particles are reasonably dispersed. In Figs. 3(a) and (b), we show the TEM images of the ReO_3@Au core–shell nanoparticles in which the Au shell is formed over ReO_3 nanoparticles of three different sizes. The core–shell nanoparticle in Fig. 3(a) is formed over a 5 nm ReO_3 particle. The core–shell nanoparticles in Fig. 3(b) are formed over 8 nm and 12 nm ReO_3 particles. The XRD pattern of the core–shell nanoparticles (see Fig. 4 (a)) matches with that of cubic gold (space group *Fm3m*, a = 4.07 Å, JCPDS-00-001-1172) establishing the presence of gold. For reasons not entirely clear to us, we did not find any reflections
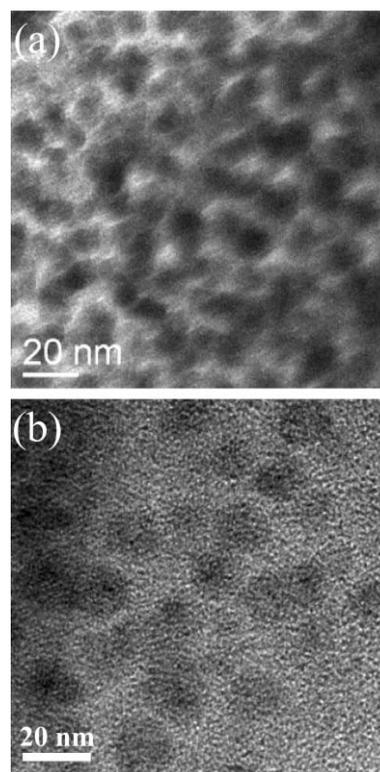
Fig. 2 TEM images of (a) ReO_3@Ag nanoparticles, and (b) ReO_3@SiO_2 nanoparticles.

of ReO_3 in the XRD patterns of the core–shell nanoparticles although the ReO_3 nanoparticles were crystalline. However, EDAX analysis (Fig. 4(b)) shows the presence of both rhenium
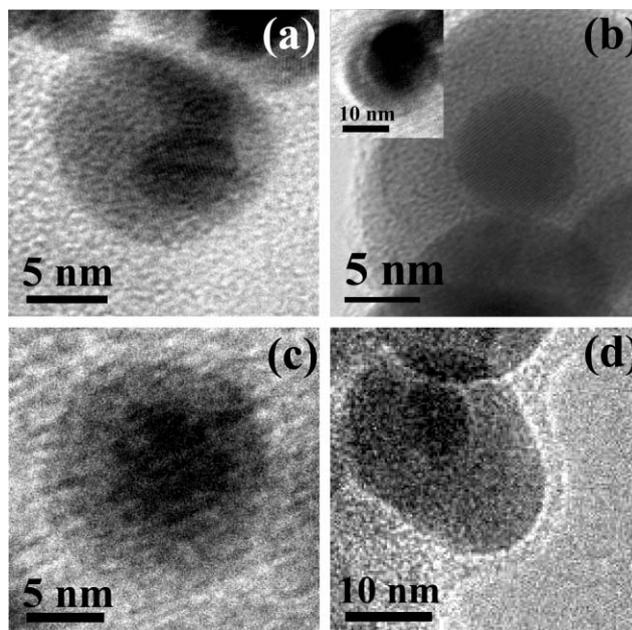
Fig. 3 TEM images of core–shell nanoparticles of (a) ReO_3@Au formed with a 5 nm ReO_3 particle, (b) ReO_3@Au formed over an 8 nm ReO_3 particle; the inset showing a core–shell nanoparticle formed over a 12 nm ReO_3 particle, (c) ReO_3@Ag formed over a 5 nm ReO_3 particle, and (d) ReO_3@Ag formed over an 8 nm particle of ReO_3.
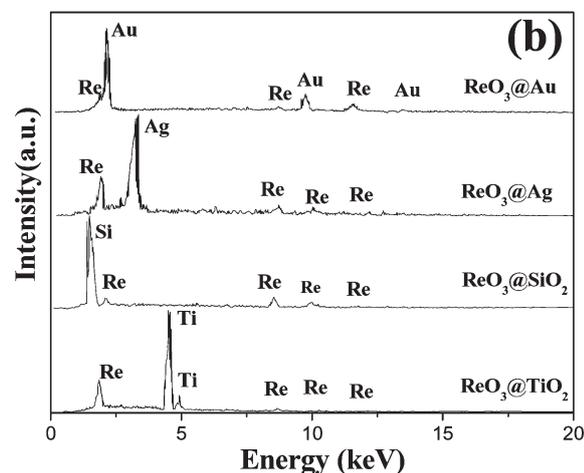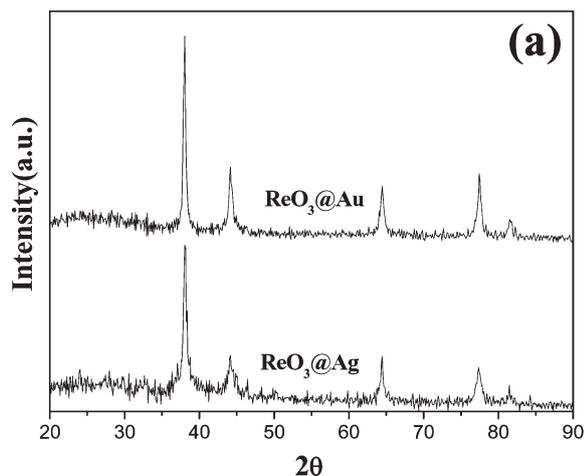
Fig. 4 (a) XRD patterns of ReO$_3$@Au and ReO$_3$@Ag core–shell nanoparticles, (b) EDAX spectra of ReO$_3$@Au, ReO$_3$@Ag, ReO$_3$@SiO$_2$ and ReO$_3$@TiO$_2$ core–shell nanoparticles.

Fig. 5 UV-vis absorption spectra of (a) ReO$_3$@Au core–shell nanoparticles (1 : 2 and 1 : 4) with a 12 nm ReO$_3$ particle, and (b) ReO$_3$@Ag core–shell nanoparticles (1 : 2 and 1 : 3) with a 12 nm ReO$_3$ particle.

and gold. Fig. 5(a) shows the UV-visible absorption spectra of ReO$_3$@Au core–shell nanoparticles with ReO$_3$: Au ratios of 1 : 2 and 1 : 4. The spectra represent composite bands comprising the plasmon absorption bands of ReO$_3$ and Au. Note that the plasmon band of the ReO$_3$ nanocrystals is around 500 nm while that of bulk gold is around 520 nm. This is the reason why the band shifts to longer wavelengths with increase in gold content of the shell. As the quantity of the shell precursor in increased, the shell thickness increases. Thus, an average shell thickness of ~3 nm was obtained in the case of ReO$_3$@Au core–shell nanoparticles when the ReO$_3$: Au molar ratio was 1 : 2, but increased to ~5 nm when the ReO$_3$: Au molar ratio was increased to 1 : 4.

TEM images of ReO$_3$@Ag core–shell nanoparticles are shown in Figs. 3(c) and (d) wherein the ReO$_3$ core particles have diameters of 5 nm and 8 nm respectively. The shell thickness obtained in case of ReO$_3$@Ag core–shell nanoparticles was ~4 nm when the ReO$_3$: Ag molar ratio was 1 : 2, and ~6 nm when the ReO$_3$: Ag molar ratio was 1 : 3. The XRD pattern (Fig. 4(a)) of the core–shell nanoparticles matches with that of cubic silver (space group *Fm3m*, *a* = 4.079 Å, JCPDS-00-001-1164). The EDAX spectrum in Fig. 4(b) shows the presence of both rhenium and silver. The

UV-visible absorption spectra of ReO$_3$@Ag core–shell nanoparticles with ratios of 1 : 2 and 1 : 3 are shown in Fig. 5(b). These spectra also represent composite bands comprising the plasmon absorption bands of ReO$_3$ and Ag. The plasmon absorption band of bulk Ag is around 420 nm. As such, we observe the broad plasmon bands shifting to lower wavelengths with increase in Ag content of the shell.

Fig. 6(a) shows a TEM image of a ReO$_3$@SiO$_2$ core–shell nanoparticle formed over an 8.5 nm ReO$_3$ particle. A shell thickness of ~4 nm was obtained for these core–shell nanoparticles when the ReO$_3$: SiO$_2$ molar ratio was 1 : 2. The shell thickness increased as the silica content was increased. The UV-visible absorption spectrum, shown in Fig. 7(a) shows a blue-shift of the ReO$_3$ plasmon band towards shorter wavelengths with increase in the SiO$_2$ content. The presence of SiO$_2$ as the shell material is confirmed by the EDAX analysis as can be seen from Fig. 4(b) which shows the presence of both rhenium and silicon. Fig. 7(b) shows photographs of the solutions of ReO$_3$@SiO$_2$ core–shell particles in ethanol revealing that the colour of the solution deepens as the proportion of SiO$_2$ is increased. Thus the formation of the ReO$_3$@SiO$_2$ core–shell particles can be

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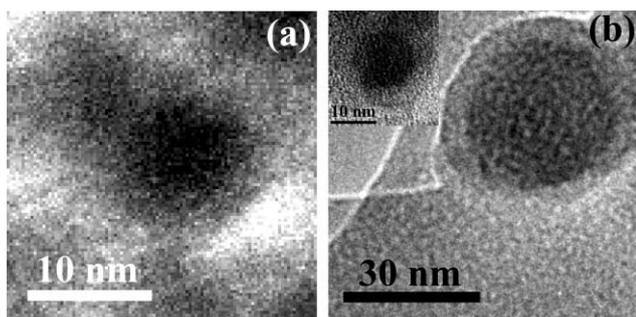
Fig. 6 (a) TEM image of a ReO$_3$@SiO$_2$ core–shell nanoparticle formed over an 8.5 nm ReO$_3$ particle, and (b) TEM image of a ReO$_3$@TiO$_2$ core–shell nanoparticle formed over a 32 nm ReO$_3$ particle with the inset showing a core–shell nanoparticle formed over a 12 nm particle of ReO$_3$.

Fig. 8 Raman spectrum of ReO$_3$@TiO$_2$ core–shell nanoparticles.

visualized by the colours of the solutions of the nanoparticles in ethanol (Fig. 7(c)).

Fig. 6(b) shows TEM images of ReO$_3$@TiO$_2$ core–shell particles formed over 32 nm and 12 nm ReO$_3$ nanoparticles. The core–shell structure is confirmed by the EDAX analysis as shown in Fig. 4(b) which shows the presence of both rhenium and titanium. Raman spectrum of ReO$_3$@TiO$_2$ core–shell nanoparticles (Fig. 8) indicate that TiO$_2$ has the anatase
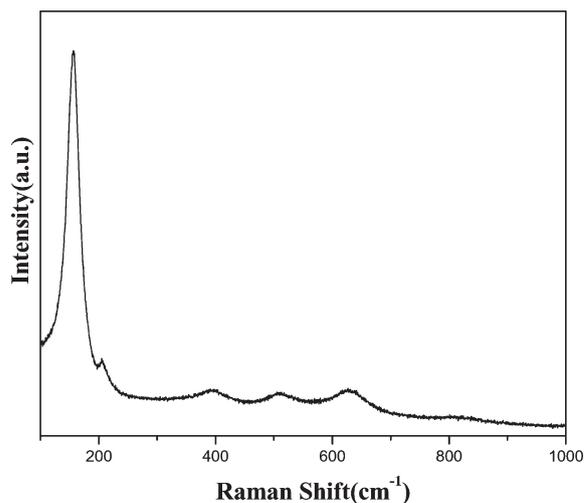
structure (although the sample is amorphous from the XRD) with characteristic bands at 138, 393, 514 and 636 cm^{-1}.[32] The UV-visible absorption spectra show a behavior similar to that of ReO$_3$@SiO$_2$ core–shell nanoparticles (Fig. 7(d)). Thus, the plasmon band is blue-shifted towards shorter wavelengths with increase in TiO$_2$ content. In case of TiO$_2$ coating, the shell
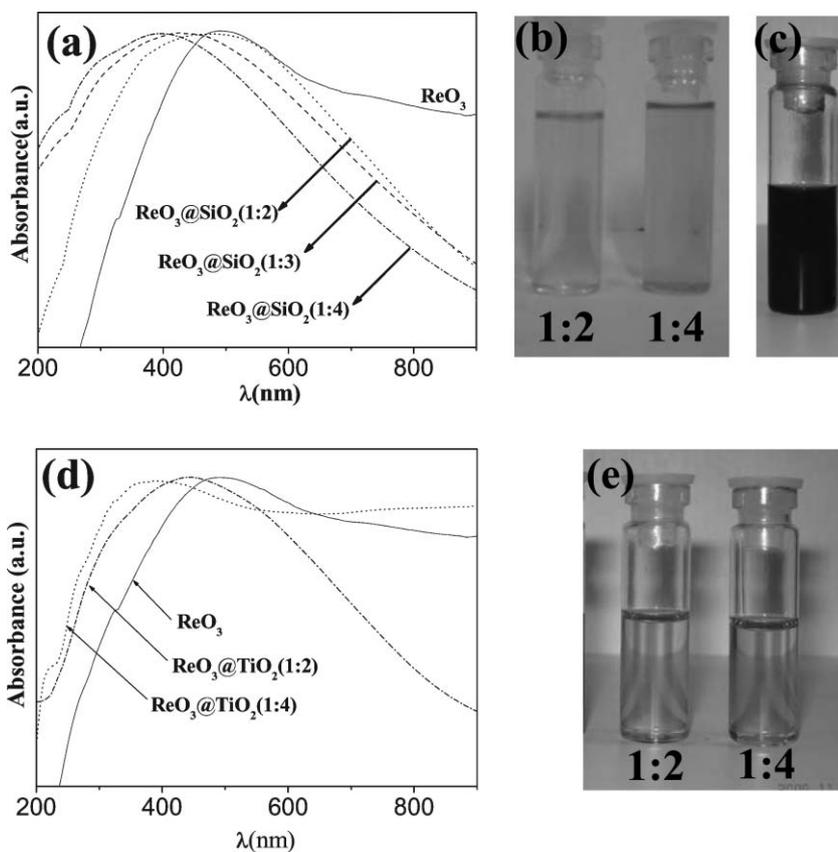
Fig. 7 (a) UV-vis absorption spectra of ReO$_3$@SiO$_2$ core–shell nanoparticles (1 : 2, 1 : 3 and 1 : 4), (b) photograph of the solutions of ReO$_3$@SiO$_2$ nanoparticles in ethanol in different molar ratios (1 : 2 and 1 : 4), (c) photograph of ReO$_3$ nanoparticle solution in ethanol, (d) UV-vis absorption spectra of ReO$_3$@TiO$_2$ core–shell nanoparticles (1 : 2 and 1 : 4), and (e) photograph of ReO$_3$@TiO$_2$ nanoparticles in DMF in different molar ratios (1 : 2 and 1 : 4).

thicknesses were ~ 5 nm and ~ 8 nm for ReO_3 : TiO_2 molar ratios of 1 : 2 and 1 : 4, respectively. The blue-shift is larger in the case of TiO_2 compared to SiO_2. This can be attributed to the higher refractive index of TiO_2 (η =2.49 for anatase phase) compared to that of SiO_2 (η = 1.45). We show photographs of $ReO_3@TiO_2$ core–shell nanoparticles in dimethylformamide in Fig. 7(d).

The blue-shift of the plasmon bands of $ReO_3@SiO_2$ and $ReO_3@TiO_2$ nanoparticles is rather unusual. Normally, when shells with high refractive index form over metal cores such as Au, the plasmon band is shifted to longer wavelengths, the shift being proportional to the refractive index of the shell material. The blue-shift observed in this case is due to excess of SiO_2 or TiO_2 present in solution after deposition on the ReO_3 nanoparticles, as pointed out earlier by Liz-Marźan.[14] The scattering from the medium is responsible for blue-shifting the plasmon absorption bands, the shift being higher in case of TiO_2.

Conclusions

In conclusion, it is possible to prepare core–shell particles around a nanoparticle of an oxide metal such as ReO_3 as the core. Thus, core–shell particles described here are indeed unique. The $ReO_3@Au$, $ReO_3@Ag$, $ReO_3@SiO_2$ and $ReO_3@TiO_2$ core–shell particles show spectra with the expected characteristics. It should be possible to prepare other core–shell nanoparticles with ReO_3 as the core e.g. $ReO_3@CdS$ and $ReO_3@CdSe$. These nanoparticles may find applications as sensors.

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