Journal of Alloys and Compounds 488 (2009) 325–327

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

A back-scattering laser Raman combination method of EFIRS and SERS to study TiO_2 nanoparticles

Rasoul Malekfar*, Nasim Mohammadian, Sara Abbasian, Fatemeh Sadeghi

Atomic and Molecular Group, Physics Department, Faculty of Basic Sciences, Tarbiat Modares University, P. O. Box 14115-175, Tehran, Islamic Republic of Iran

ARTICLE INFO

Article history:
Received 5 November 2008
Received in revised form 23 August 2009
Accepted 25 August 2009
Available online 31 August 2009

Keywords:
TiO_2 nanoparticles
Electric field
Raman scattering
SERS
EFIRS

ABSTRACT

For the first time, we believe, a combination effect of Surface Enhanced Raman Scattering (SERS) and Electric Field Induced Raman Scattering (EFIRS) has been used to study TiO_2 nanocrystallites. This method can be widely used to obtain phononic properties of materials. To investigate this combination effect for TiO_2 nanoparticles, silver colloid has been used. In some cases when SERS technique shows no Raman mode intensity enhancement, our present procedure leads to the enhancement of Raman scattering by an order of four times in magnitude. This phenomenon occurs because external electric field affects on silver nanoparticles and can give rise to the polarization of nanoparticles and creates large local electric fields on their surfaces.

1. Introduction

TiO_2 nanocrystallites, are semiconductors with a wide energy gap of about 3.2 eV. As a new material, it has many excellent applications in photocatalysis, photochemical solar cells, gas sensors, white pigment materials, microelectronic devices, etc. [1]. Therefore recently, TiO_2 nanoparticles are the subject of intensive scientific researches. These nanoparticles have many polymorphs, among them anatase, rutile and brookite are of naturally grown phases. Both anatase and rutile belong to the same crystal symmetry (tetragonal), while brookite has orthorhombic crystal structure [2].

In recent years the Electric Field Induced Raman Scattering (EFIRS) has become an attractive tool to probe the changes in the electric fields in space–charge layers at semiconductor surfaces and interfaces [3,4]. EFIRS can cause either an enhancement of the lattice allowed modes or an activation of theoretically forbidden modes. The influence of EFIRS has previously been examined for some semiconductors such as ZnO, GaAs, and CdS. It can be claimed that the external electric fields can significantly influence phonon modes in semiconductors and its piezoelectric characteristics [5,6].

On the other hand, Surface Enhanced Raman Scattering (SERS) is a very powerful Raman technique, being able to provide a spectral intensity enhancement by orders of magnitude [7]. The phenomenon originates from coupled optical responses of plasmonic metals such as Ag and of molecules located on or in a close proximity of their surfaces. The nanostructures can be nanoparticles, nanowires or other nanostructured materials. In such coupled systems, both the incident light and the inelastic scattered light (Raman) by adsorbed molecules are enhanced by resonance Mie scattering of light by the plasmonic metal nanostructures [8].

In this research we investigate, we believe for the first time, SERS and EFIRS effects, due to their similarity in enhancement of Raman modes intensity. The combination of SERS and EFIRS effects has been applied to TiO_2 nanoparticles in pellet disk and also solution shapes. This combination effect is more sensitive than simple SERS effect and it can be used to study the phononic characteristics and lattice vibrational properties of TiO_2 nanoparticles.

2. Experimental

2.1. Synthesis of TiO_2 nanoparticles

TiO_2 nanocrystallites in anatase phase were synthesized by sol–gel method at room temperature. In this way, four materials consisting of tetrabutyl titanate [$Ti(OBu)_4$], ethanol, H_2O and HCl were used. In order to gain the best nanostructure and morphology, the following molar ratio was applied:

$$Ti(OBu)_4 : EtOH : HCl : H_2O = 1 : 15 : 0.3 : 4$$

Under constant stirring condition tetrabutyl titanate [$Ti(OBu)_4$] and mixture of HCl and de-ionized water was added to ethanol. After the gelation, the wet gel was dried and the collected powders were annealed at 450 °C for 2 h to obtain TiO_2 nanocrystallites. A very typical X-ray diffraction pattern of the synthesized TiO_2 nanoparticles has been presented in Fig. 1.

* Corresponding author. Tel.: +98 21 8288 3440; fax: +98 21 8288 3440.
E-mail address: Malekfar@Modares.ac.ir (R. Malekfar).

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doi:10.1016/j.jallcom.2009.08.121

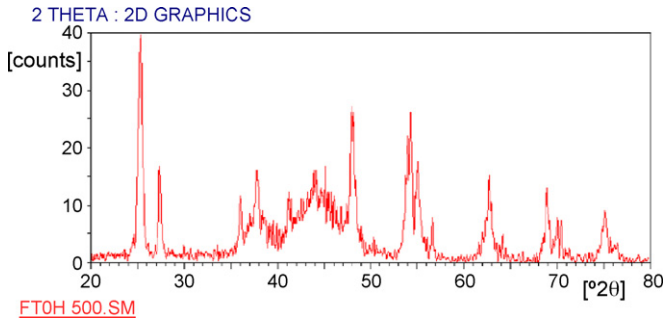

Fig. 1. A typical X-ray diffraction pattern of the synthesized TiO_2 nanoparticles.

2.2. Preparation of silver colloid

Silver colloid was prepared according to Lee and Meisel's method [9]. In 500 ml of de-ionized water, 90 mg of silver nitrate was dissolved and the solution was heated to boiling. Then 10 ml of a 1% trisodium citrate aqueous solution was added into the boiling silver nitrate solution drop-wise, accompanied by vigorous stirring. The mixed solution was kept boiling for a further 10 min. Finally, a green–gray silver colloid was obtained, which was stable for several days or weeks [10].

2.3. Preparation of samples

In order to investigate the effects of high DC electric field on Surface Enhanced Raman Scattering (SERS) spectra, the synthesized TiO_2 nanoparticles were pressed into a pellet disk shape with a 10 mm diameter and 2 mm thickness and the rest of them were dispersed in methanol to achieve solution of 0.1 M of TiO_2 nanoparticles.

The mixture of TiO_2 nanoparticles and methanol was uniformly added drop-wise to a layer of quantitative filter paper and then it was dried for about 10 min. By continuing and adding more silver colloid onto both filter paper and the pellet and leaving them to dry, the samples for experiment were obtained.

2.4. Instrumentation

Back-scattering Raman spectra of the prepared samples at high DC electric fields were recorded. A schematic of the experimental set-up is shown in Fig. 2. Electric fields were applied at two directions of parallel and perpendicular to the axis of the pellet. Raman experiments were conducted at room temperature in a back-scattering geometry by using a Thermo Nicolet Almega Raman spectrometer system with a 532 nm light emitted as the second harmonic from a Nd:YLF laser. The laser power was set to about 30 mW at the surface of the sample. The exposure time was 4 s with a spectral resolution of 4 cm^{-1}.

3. Results and discussion

A series of typical back-scattering Raman spectra of TiO_2 nanocrystallites pellets that was smeared with silver colloid, under the effect of high DC external electric fields have been presented in Fig. 3. The three Raman peaks at 424 cm^{-1}, 670 cm^{-1} and 547 cm^{-1} are assigned to the $B_{1g}(1)$, $E_g(3)$ and doublet of A_{1g} plus $B_{1g}(2)$ modes of anatase phase, respectively [11].

As it is shown in Fig. 3, the lower bottom Raman spectrum shows the spectrum of the TiO_2 nanocrystallite pellet without silver colloid coating. The other three spectra at the top shown in Fig. 3 are related to the silver colloid coated samples, as SERS, EFIRS and combined SERS/EFIRS effects. By comparing different back-scattering Raman spectra presented in Fig. 3, it can be concluded that no enhancement in the Raman spectra has occurred, but in the top spectrum shown in Fig. 3, which is related to the combination of SERS and EFRIS effects, a significant increase and enhancement in the Raman modes intensity are observed.

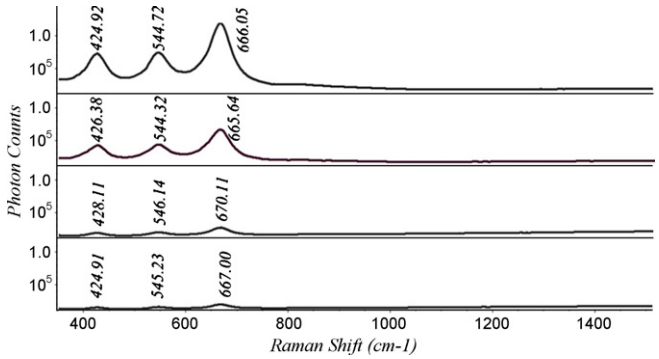

Fig. 3. Combination effects of SERS and EFIRS and the spectra of anatase phase TiO_2 tablet. Bottom spectrum: without silver colloid coating and at 0 kV cm^{-1}; second spectrum from bottom: with silver colloid coating and at 0 kV cm^{-1}; second spectrum from top: with silver colloid coating at 6 kV cm^{-1}; top spectrum: with silver colloid coating and at 14 kV cm^{-1}.

The intensity enhancement in the Raman modes indicates a strong interaction among the metal nanoparticles and the surface phononic modes which causes quite a different derivative of the polarizability tensor of the molecule [10]. In fact at the plasmon frequency, the metal nanoparticles can be polarized resulting a large field-induced polarization and also large local electric fields on the surface. These local electric fields increase the Raman scattering intensity, which is proportional to the square of the applied electric field on the molecule [12–14].

As a result, the effective electric field experienced by the molecule, and in the mentioned configuration, is much larger than the actual applied electric field.

Back-scattering Raman spectra of the synthesized TiO_2 nanocrystallites on the filter paper samples under the effect of high DC external electric fields are presented in Fig. 4. In this figure it is obvious that in the absence of applied electric field, no enhancement in the intensity of Raman modes was observed (Fig. 4, the two bottom spectra). However, the combination of SERS and EFIRS, on a pellet disk shape sample, gives rise to the amplification of Raman modes intensity (Fig. 4, the two top spectra). Therefore the

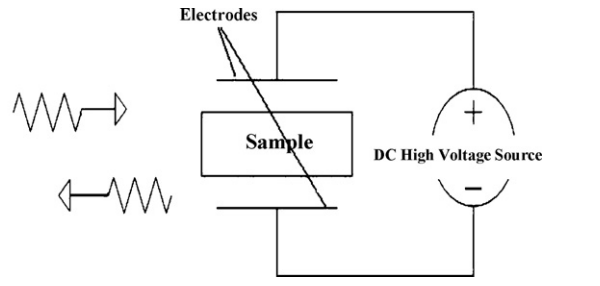

Fig. 2. A schematic of the experimental set-up used in this research. The back-scattering Raman scattering spectrometer with its CCD detector is shown in the left and the sample cell, its surrounded electrodes and the DC high voltage source are presented in the right.

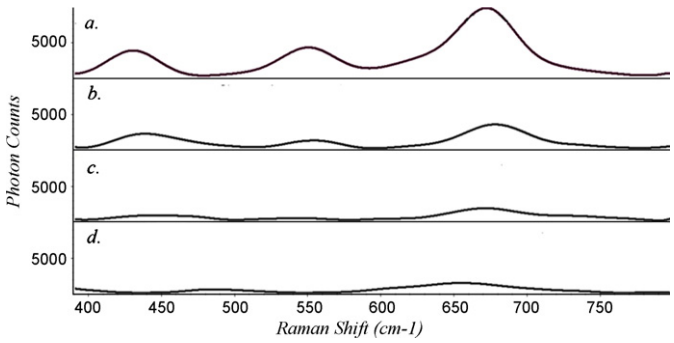

Fig. 4. Combination effects of SERS and EFIRS and the spectra of 0.1 M solution of TiO_2 on the silver-coated filter paper. Bottom spectrum: without silver colloid and at 0 kV cm^{-1}; second spectrum from top: with silver colloid and at 0 kV cm^{-1}; second spectrum from top: with silver colloid 6 kV cm^{-1}; top spectrum: with silver colloid and at 14 kV cm^{-1}.

external electric field has given rise to both enhancing effect of electric field on the surface of Ag nanoparticles and also surface polarization. Increasing polarization of metal nanoparticles in silver colloid solution results in enhancing local electric fields on the material surface. This is in complete agreement with the results of the spectra presented in Fig. 3 in which the spectral analysis shows that there is a strong proportionality between the Raman mode intensity enhancement and morphology of the Ag nanoparticles assembly. Moreover no new mode or induced shift by the combination of SERS and EFIRS effects was observed in our experiment results.

4. Conclusions

In summary, TiO_2 nanoparticles and silver colloid were made by sol–gel and citrate reduction methods, respectively. Experimental results show that the Surface Enhanced Raman Scattering effects in external electric field and combined SERS and EFIRS effects, are much more effective on increasing Raman modes intensity. Furthermore, this method can be used as a probe technique for monitoring the synthesis quality of TiO_2 nanoparticles with significant higher sensitivity than SERS method.

References

[1] J.-Y. Zhang, et al., Non-Cryst. Solids 303 (2002) 134.
[2] P. Madhu Kumar, S. Badrinarayanan, Murali Sastry, Thin Solid Films 358 (2000) 12.
[3] T.S. Jeong, C.J. Youn, J. Korean Phys. Soc. 49 (4) (2006) 1510.
[4] F.K. Shan, et al., J. Korean Phys. Soc. 42 (2003) S1174.
[5] R.P. Wang, et al., Thin Solid Films 411 (2002) 69.
[6] Y.J. Geurts, Surf. Sci. Rep. 18 (1993) 1.
[7] E. Perevedentseva, et al., Surf. Sci. 600 (2006) 3723.
[8] B. Vlckova, et al., Mol. Struct. 834–836 (2007) 42.
[9] P.C. Lee, D. Meisel, J. Phys. Chem. 86 (1982) 3391.
[10] Z. Niu, Y. Fang, Colloid Interface Sci. 303 (2006) 224.
[11] G.A. Samara, P.S. Peercy, Phys. Rev. B 7 (3) (1973) 1131.
[12] V.-D. Tuan, Trends Anal. Chem. 17 (1998) 557.
[13] L. Zhang, P. Zhang, Y. Fang, Anal. Chim. Acta 591 (2007) 214.
[14] G. Maroulis, Atoms, Molecules and Clusters in Electric Fields, Imperial College Press, London, 2005.