Facile size-controlled preparation of highly photocatalytically active praseodymium zirconate nanostructures for degradation and removal of organic pollutants

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Abstract Highly photocatalytically active praseodymium zirconate ($\text{Pr}_2\text{Zr}_2\text{O}_7$) nanostructures were prepared by a new simple route with praseodymium nitrate and zirconyl nitrate as praseodymium and zirconium sources (at lower temperature). Benzene tricarboxylic acid as new stabilization agent and capping agent in presence of propylene glycol as connecting agent were applied to fabricate the nanostructured praseodymium zirconate for the first time. The as-obtained nanostructured $\text{Pr}_2\text{Zr}_2\text{O}_7$ was analyzed by UV–vis diffuse reflectance spectroscopy, energy dispersive X-ray microanalysis (EDX), Fourier transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), photoluminescence (PL) spectroscopy, field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). Results of this investigation reveal that grain size, purity and shape of the $\text{Pr}_2\text{Zr}_2\text{O}_7$ are controlled by altering preparation factors such as the kind of stabilization agent and alkaline agent. This is first attempt on the study of photocatalytic performance of the nanostructured praseodymium zirconate in various conditions. The effect of various factors including kind of pollutant, grain size of praseodymium zirconate nanostructures, praseodymium zirconate dosage and kind of illumination light on photocatalytic behavior of products were evaluated.

Keywords: $\text{Pr}_2\text{Zr}_2\text{O}_7$; Photocatalytic activity; Nanostructure; Electron microscopy.

1. Introduction

...Praseodymium zirconate ($\text{Pr}_2\text{Zr}_2\text{O}_7$), which belongs to the class of rare earth-doped zirconium oxide materials, has been widely applied in high-temperature fuel cell, gas turbines, proton solubility, diesel engines, fluorescence centers and photocatalyst [1-5] owing to its specific and striking properties [6-9]. Up to now, synthetic methods such as complex precipitation, solid-state reaction, sol-gel, hydrothermal, sol-gel combined electrospinning and citrate gel have been reported for the fabrication of rare earth-doped zirconium oxide nanomaterials [10-17].

It is well known that the grain size and shape have a great impact on the behavior and final utilizations of the nanoscale materials. Hence, several preparation approaches have been introducing for grain size and shape controlling of nanoscale materials [18-24]. Among of different approaches of production of nanoscale materials, the Pechini way is well-known as a useful, cost-effective and simple process for grain size and shape controlling of nanoscale materials.

This work reports a new simple way to prepare the nanostructured praseodymium zirconate with the aid of praseodymium nitrate and zirconyl nitrate and benzene tricarboxylic acid as new stabilization agent and capping agent in presence of propylene glycol as connecting agent. To our knowledge, it is the first time that benzene tricarboxylic acid as stabilization agent and capping agent in presence of propylene glycol as connecting agent are employed for the production of nanostructured praseodymium zirconate and the effect of factors such as the kind of stabilization agent and alkaline agent on the grain size, purity and shape of the nanostructured praseodymium zirconate by a new simple approach are investigated.

Today, water purification is known as one of the most significant fields in scientific research and organic dyes are the major contaminant kinds of wastewater. To date, much effort has been devoted to diminish or destruction of organic contaminants in the wastewater. Utilizing of photocatalysts is known as one of the most useful and promising routes for elimination organic contaminants from water [25-29].

This work is the first attempt on the study of photocatalytic performance of the nanostructured praseodymium zirconate in various conditions. The ability for the degradation of the organic contaminants including rhodamine B, methylene blue, methyl orange and eosin Y (as the model contaminants) were examined by photocatalysis experiments. The effect of various factors including kind of pollutant, grain size of praseodymium zirconate nanostructures, praseodymium zirconate dosage and kind of illumination light on photocatalytic behavior of products were evaluated.

2. Experimental

2.1. Materials and characterization

All the chemicals for the preparation of $\text{Pr}_2\text{Zr}_2\text{O}_7$ nanostructures including praseodymium nitrate, zirconyl nitrate, propylene glycol, citric acid, salicylic acid, ethylenediamine, succinic acid, propylenediamine, maleic acid, benzene tricarboxylic acid, liquor ammonia solution containing 25% ammonia and trimethylamine were purchased from Merck Company and were applied without additional purification. Transmission electron microscope (TEM) images of as-obtained praseodymium zirconate nanostructures were taken on a JEM-2100 with an accelerating voltage of 200 kV. Fourier transform infrared spectra of as-prepared products were obtained on a Shimadzu Varian 4300 spectrophotometer in KBr pellets in the $400\text{--}4000\text{ cm}^{-1}$ range. Thermogravimetric-differential thermal analysis (TG-DTA) of the as-obtained sample was done by employing a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 ml min^{-1} and a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The EDS analysis of the as-produced praseodymium zirconate nanostructures was carried out by employing a Philips XL30 microscope. The UV-vis diffuse reflectance spectrum of the as-produced praseodymium zirconate nanostructures was obtained on a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan). Powder X-ray diffraction (XRD) patterns of the as-synthesized praseodymium zirconate nanostructures were recorded by applying a diffractometer of Philips Company with X'PertPromonochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$).

FESEM images of praseodymium zirconate nanostructures were visualized by employing a Tescan mira3 field emission scanning electron microscope (FESEM).

2.2. *Preparation of praseodymium zirconate nanostructures*

Praseodymium zirconate were prepared by a new simple route. In a typical experiment, 1 mmol of praseodymium nitrate and 1 mmol of zirconyl nitrate were dissolved in distilled water. Then 2 mmol of benzene tricarboxylic acid was added to the mixed solution and the pH of the resultant solution was adjusted to 6 by adding ammonia solution drop-wise. Then, 1.2 mmol of propylene glycol as esterification agent was added the solution. Evaporation of the gel-like solution leads to the preparation of porous solid mass which was ground in the agate mortar applying acetone. The prepared powders were heated at 350 °C for 3 h and then at 800 °C for 5 h (sample no. 5). Schematic diagram of the synthesis of the nanostructured praseodymium zirconate is demonstrated in Fig. 1. The influences of factors such as the kind of stabilization agent and alkaline agent on the shape, purity and grain size of the nanostructured praseodymium zirconate were examined (Table 1).

2.3. *Photocatalytic tests*

The photocatalytic performance of as-synthesized praseodymium zirconate nanostructures was evaluated by employing of the various contaminants solution. The solution comprising the 50 mg of the praseodymium zirconate nanostructures and 5 mg of the contaminant in the quartz reactor was employed to examine the photocatalytic behaviour. After aerating for 1/2 h, the mixture was subjected to the illumination of the UV or visible light. The influence of various factors including kind of pollutant, grain size of praseodymium zirconate nanostructures, praseodymium zirconate dosage and kind of illumination light on photocatalytic behavior of products were evaluated. The contaminant photodegradation efficiency was calculated as follow:

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_t and A_0 are the absorbance quantity of contaminant solution at t and 0 min by a UV-vis spectrometer, respectively.

3. Results and discussion

...Thermogravimetry (TG) and derivative thermogravimetry (DTG) techniques were applied to examine the thermal stability of the as-produced powders (sample no. 8 before calcination steps). Fig. 2 reveals the TG/DTG curve of as-synthesized powders (sample no. 8 before calcination steps). In this figure, there are three mass loss stages. The happened endothermic weight loss in the temperature range of 25-160 °C (indicating 16.33 % weight loss) corresponds to the dehydration and depolymerisation of the polymeric residual in the as-synthesized powders. Two happened endothermic stages at the temperature range of 160-800 °C (showing 58.42 % weight loss) may be related to complex decomposition and polymeric resin combustion as well as removal of the nitrates and residual carbonate intermediate and demonstrate the preparation of praseodymium zirconate nanostructures.

Fig. 3a and b exhibits the infrared spectra of the as-produced powders (sample no. 8 before calcination steps) and as-obtained praseodymium zirconate nanostructures (sample no. 8), respectively. The bands located at 1599, 1385 and 1046 cm^{-1} in the Fig. 3a may correspond to the vibration of C=O and the stretching vibration of COO^- and C-O, respectively [30]. The bands appear at 1129, 922 and 834 cm^{-1} in the Fig. 3a belong to C-C-O stretching vibration of propylene glycol [31]. The bands centered at 683 and 551 cm^{-1} (Fig. 3a) may correspond to the N-O stretching vibration of the nitrates and C-O vibration of the propylene glycol [31]. The band located at 3433 cm^{-1} in the FT-IR spectrum of the as-produced praseodymium zirconate nanostructures (sample no. 8) belongs to the $\nu(\text{OH})$ stretching vibration of physisorbed water molecules (Fig. 3b) [23]. The characteristic peak of the praseodymium zirconate nanostructures appears at 400 cm^{-1} [32] (Fig. 3b).

To examine the elemental composition of the as-synthesized praseodymium zirconate nanostructures (sample no. 8), the EDS analysis was done. Fig. 4 reveals that the elements in this sample are Pr, Zr and O only.

To identify the crystalline structure, mean crystallite size and composition of the as-produced nanostructured samples, XRD technique was utilized. Fig. 5a-g depicts XRD patterns of the sample nos. 1, 2, 3, 4 and 5 prepared applying salicylic acid, maleic acid, succinic acid, citric acid and benzene tricarboxylic in presence of ammonia as well as sample nos. 6, 7 and 8 synthesized utilizing trimethylamine, ethylenediamine and propylenediamine in presence of benzene tricarboxylic, respectively. XRD results reveal that the sample nos. 1 and 3 consist of the ZrO_2 and Pr_6O_{11} as well as the sample nos. 2, 4 and 6 containing the Pr_6O_{11} , and that the pure praseodymium zirconate nanostructures have not been formed (Fig. 5a-d and f). By applying ammonia and propylenediamine as basic agent in presence of benzene tricarboxylic as chelating agent, pure praseodymium zirconate nanostructures have been prepared (Fig. 5e and g). All diffraction peaks in the XRD patterns (Fig. 5e and g) can be attributed to the cubic phase of $\text{Pr}_2\text{Zr}_2\text{O}_7$ (JCPDS Card file no. 19-1021). By applying Scherrer equation [24], the mean crystallite size of the as-produced praseodymium zirconate nanostructures (sample nos. 5 and 8) from the XRD results in Fig. 5e and g were determined to be about 20 and 17 nm.

FESEM technique was applied to evaluate the influence of factors such as the kind of stabilization agent and alkaline agent on the grain size and shape of the praseodymium zirconate nanostructures. For studying the influence of the kind of stabilization agent on the shape and grain size of the praseodymium zirconate, the five different carboxylic acids as chelating agent including salicylic acid, maleic acid, succinic acid, citric acid and benzene tricarboxylic acid in presence of propylene glycol as connecting agent were utilized (sample nos. 1-5). Fig. 6 and 7 depicts FESEM images of sample nos. 1-5 synthesized in the presence of the salicylic acid (Fig. 6a and b), maleic acid (Fig. 6c and d), succinic acid (Fig. 6e and f), citric acid (Fig. 7a and b) and benzene tricarboxylic acid (Fig. 7c and d). As illustrated in Fig. 6 and 7, by utilizing five different carboxylic acids, the nanoparticles are prepared. Among these synthesized samples, sample no. 5 prepared by applying benzene tricarboxylic acid show homogeneous sphere-like nanoparticles with small particle size (Fig. 7c and d). It seems that among these employed carboxylic acids as stabilization agent (Fig. 8), benzene tricarboxylic acid can provide

the highest steric hindrance influence. Benzene tricarboxylic acid can act as both stabilization agent and capping agent through impeding from the aggregation of the produced nanoparticles (Fig. 7c and d). Besides, FESEM images indicate that the enhancement in the steric hindrance influence causes to the grain size of samples becomes small (Fig. 6 and 7). It seems that the nucleation to be happened rather than the particle growth through enhancing the steric hindrance effect. From the XRD and FESEM results, it was found that benzene tricarboxylic acid was the best stabilization agent type for pure praseodymium zirconate nanostructures with uniform sphere-like shape and small particle size (Fig. 7c and d).

...For examining the effect of the kind of alkaline agent on the shape and grain size, the sample nos. 6, 7 and 8 were prepared by utilizing benzene tricarboxylic acid in the presence of the trimethylamine, ethylenediamine and propylenediamine, respectively. Fig. 9a-e indicates FESEM image of the sample nos. 6, 7 and 8. Among these employed alkaline agents, propylenediamine has the highest steric hindrance influence (Fig. 8). The propylenediamine can act as both alkaline agent and co-capping agent through hindering the aggregation of the produced nanoparticles. As demonstrated in Fig. 7c and d and 9a-e, through enhancing steric hindrance effect, the amount of uniform sphere-like nanoparticles increased. When propylenediamine was used, very uniform spherical praseodymium zirconate nanoparticles with fine grain size were produced (Fig. 9e). These results reveal that propylenediamine as co-capping agent owing to its high steric hindrance influence can control the shape and grain size of praseodymium zirconate. It is apparent that the applying benzene tricarboxylic acid in presence of propylenediamine brings about that pure cubic praseodymium zirconate nanostructures with uniform spherical shape and fine grain size are produced (Fig. 5g and 9e).

To elucidate the more details of shape and grain size of the praseodymium zirconate nanostructures prepared by applying benzene tricarboxylic acid in presence of propylenediamine (sample no. 8), TEM analysis was performed. The TEM images (Fig 10a-c) indicate that quasi-spherical praseodymium zirconate nanoparticles with diameter in range of 7-23 nm are sintered together.

To assess the optical features of the as-synthesized praseodymium zirconate nanostructures, PL and UV–vis diffuse reflectance spectra were recorded. The PL spectrum of praseodymium zirconate sample (prepared by applying benzene tricarboxylic acid in presence of propylenediamine) was obtained by the excitation wavelength of 300 nm, as illustrated in Fig. 11a. This spectrum reveals an emission band appears at 390 nm. This emission band may correspond to charge transition from the 4f band to the valence band of praseodymium zirconate.

...Fig. 11b exhibits the UV–vis absorption spectrum of sample no. 8 (prepared by applying benzene tricarboxylic acid in presence of propylenediamine). In this UV–vis absorption spectrum, the absorption peak appears at 358 nm. It is generally accepted that the band gap (E_g) has a striking impact on the identifying the features of the nanoscale compounds employed as photocatalyst and is mostly estimated from the UV–vis diffuse reflectance results. The E_g value can be calculated based on the UV–vis diffuse reflectance results by applying Tauc's formula [20]. The E_g value of the praseodymium zirconate nanostructures was obtained through extrapolating the linear section of the plot of $(ah\nu)^2$ against $h\nu$ to the energy axis (Fig. 11c). The E_g value of the as-produced praseodymium zirconate nanostructures estimated to be 3.25 eV. From the calculated E_g value, as-produced praseodymium zirconate sample may be employed as the photocatalyst.

...The influence of various factors including kind of pollutant, grain size of praseodymium zirconate nanostructures, praseodymium zirconate dosage and kind of illumination light on photocatalytic behavior of products were evaluated through monitoring the photodegradation of water contaminants in an aqueous solution. Fig. 12a depicts the influence of various cationic (rhodamine B and methylene blue) and anionic (methyl orange and eosin Y) contaminants on photocatalytic behavior of the prepared praseodymium zirconate nanostructures. It is apparent that (Fig. 12a) the photocatalytic behavior of cationic contaminants is better than anionic contaminants. The decomposition efficiency of methyl orange, eosin Y, methylene blue and rhodamine B are 46, 51, 86 and 88%, respectively. These results demonstrate that in photocatalytic decomposition process, the cationic contaminant adsorption on the praseodymium zirconate is higher than the amount of adsorption of anionic

contaminant on it. The nanostructured praseodymium zirconate has oxygen atoms with a great electron density on its surface. It seems that praseodymium zirconate with negative charge can adsorb the cationic contaminants with positive charge [33]. The greatest amount of photocatalytic decomposition is for rhodamine B as cationic contaminant.

The photocatalytic behavior of the prepared praseodymium zirconate nanostructures (sample nos. 5 and 8) were compared by the photodegradation of rhodamine B contaminant, as depicted in Fig. 12b. No rhodamine B was practically decomposed after 50 min without employing UV light illumination or as-produced praseodymium zirconate samples. This observation demonstrated that the contribution of self-degradation was insignificant. The praseodymium zirconate nanostructures indicate obvious photocatalytic activity to rhodamine B contaminant under UV light illumination (Fig. 12b). The photocatalytic performance of sample no. 8 is evidently better than sample no. 5 (Fig. 12b). Utilizing photocatalytic calculations by Eq. (1), the rhodamine B contaminant degradation efficiency was about 88% by sample no. 8 and 76% by sample no. 5 after 50 min illumination of UV light. Based on the results and particle size of samples, the sample no. 8 with smaller particle size (Fig. 9e) that has larger surface area demonstrates the higher efficiency for decomposition in comparison to sample no. 5 (Fig. 7c and d). Thus particle size of nanostructures is a key parameter on decomposition of water contaminant by applying photocatalyst. The sample no. 8 with smaller particle size because of large surface area demonstrates higher photocatalytic activity. By reducing grain size of photocatalyst, the surface area to volume ratio, accessible surface active sites as well as interfacial charge carrier transfer amounts enhanced and hence leading to better catalytic performance.

The influence of the dosage of the nanostructured praseodymium zirconate (sample no. 8) on the methylene blue decomposition is illustrated in Fig. 12c. By enhancing praseodymium zirconate dosage, the methylene blue decomposition is enhanced. The results demonstrate that the percentage decomposition of methylene blue under UV illumination changed from 86% to 90% with changing amount of praseodymium zirconate from 25 to 75 mg.

The photocatalytic behavior of the nanostructured praseodymium zirconate with 75 mg amount in the initial step (0-30 min) is slower than the other amounts. Based on the photocatalytic performance results, it is found that slower performance can be owing to enhancing of praseodymium zirconate quantity, opacity of mixture and reducing of absorption of UV illumination. Furthermore, owing to similarity of ultimate decomposition percentage for 75 and 50 mg of praseodymium zirconate nanostructures and slower photocatalytic performance of 75 mg loading in the initial step (0-30 min), the best praseodymium zirconate loading is 50 mg.

The photocatalytic behavior of the nanostructured praseodymium zirconate (sample no. 8) under UV and visible light illumination were also compared. Fig. 12d depicts the obtained results. The nanostructured praseodymium zirconate is illuminated by visible light have relatively fine degradation efficiency (68%) for methylene blue contaminant. The methylene blue decomposition under UV illumination is better than visible illumination, as illustrated in Fig. 12d.

The suggested mechanism of the photocatalytic degradation of the methylene blue may be assumed as:

The decomposition mechanism of contaminant for the nanostructured praseodymium zirconate is depicted in Fig. 13a.

The applied praseodymium zirconate in this study is stable after photocatalytic performance. Fig. 13b presents XRD pattern of the nanostructured praseodymium zirconate after photocatalytic performance. By comparing of XRD patterns of the nanostructured praseodymium zirconate (sample no. 8) before and after photocatalytic performance (Figs. 5g and 13b), it is apparent that the nanostructured praseodymium zirconate as photocatalyst is stable.

These results demonstrate that the as-produced praseodymium zirconate nanostructures (sample no. 8) have high potential to be employed as a novel, suitable and desirable type of photocatalyst under UV and visible illumination for removal of cationic contaminants.

4. Conclusions

This work describes a new simple approach to synthesize praseodymium zirconate nanostructures with the aid of praseodymium nitrate and zirconyl nitrate as praseodymium and zirconium sources and benzene tricarboxylic acid as stabilization agent and capping agent in presence of propylene glycol as connecting agent. Applying of propylene glycol as connecting agent in presence of benzene tricarboxylic acid as stabilization agent is the novelty of this study. By altering the kind of stabilization agent and alkaline agent, we could produce praseodymium zirconate nanostructures with very homogeneous sphere-like shape and with fine grain size. This study demonstrates that benzene tricarboxylic acid in presence of propylenediamine is an extremely good choice for preparation of pure praseodymium zirconate nanostructures with small particle size. To the best of our knowledge, this is first attempt on the study of photocatalytic performance of praseodymium zirconate nanostructures. Furthermore, the influence of various factors including kind of pollutant, grain size of praseodymium zirconate nanostructures, praseodymium zirconate dosage and kind of illumination light on photocatalytic behavior of products were evaluated. The results demonstrate that the as-produced praseodymium zirconate nanostructures have high potential to be employed as a novel, suitable and desirable type of

photocatalyst under UV and visible illumination for removal of cationic contaminants. This present approach provides a novel, convenient and facile process for the production of praseodymium zirconate nanostructures (at lower temperature).

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Table 1 The preparation conditions of the praseodymium zirconate synthesized in this study.

Sample No.	Stabilization agent type	Alkaline agent	Figure of XRD patterns	Figure of FESEM images
1	Salicylic acid	Ammonia	5a	6a and b
2	Maleic acid	Ammonia	5b	6c and
3	Succinic acid	Ammonia	5c	6e and f
4	Citric acid	Ammonia	5d	7a and b
5	Benzene tricarboxylic acid	Ammonia	5e	7c and d
6	Benzene tricarboxylic acid	Trimethylamine	5f	9a and b
7	Benzene tricarboxylic acid	Ethylenediamine	-	9c and d
8	Benzene tricarboxylic acid	Propylenediamine	5g	9e

Figure Captions:

Figure 1. Schematic diagram of the preparation of the praseodymium zirconate nanostructures.

Figure 2. TG/DTG curve of as-synthesized powders (sample no. 8 before calcination steps).

Figure 3. FT-IR spectra of the as-produced powders (sample no. 8 before calcination steps) (a) and as-obtained praseodymium zirconate nanostructures (sample no. 8) (b).

Figure 4. EDS pattern of the praseodymium zirconate nanostructures (sample no. 8).

Figure 5. XRD patterns of the sample nos. 1, 2, 3, 4 and 5 prepared applying salicylic acid (a), maleic acid (b), succinic acid (c), citric acid (d) and benzene tricarboxylic (e) in presence of ammonia as well as sample nos. 6 and 8 synthesized utilizing trimethylamine (f) and propylenediamine (g) in presence of benzene tricarboxylic, respectively.

Figure 6. FESEM images of the sample nos. 1-3 synthesized in the presence of the salicylic acid (a and b), maleic acid (c and d), succinic acid (e and f).

Figure 7. FESEM images of the sample nos. 4 and 5 synthesized in the presence of the citric acid (a and b) and benzene tricarboxylic acid (c and d).

Figure 8. Various carboxylic acids applied as chelating agent and different alkaline agents.

Figure 9. FESEM images of the sample nos. 6-8 were prepared by utilizing benzene tricarboxylic acid in the presence of the trimethylamine (a and b), ethylenediamine (c and d) and propylenediamine (e).

Figure 10. TEM images of the praseodymium zirconate nanostructures (sample no. 8).

Figure 11. PL spectrum (a) and UV-vis diffuse reflectance spectrum (b) of the as-prepared praseodymium zirconate nanostructures (sample no. 8) and the curve of $(\alpha h\nu)^2$ against $h\nu$ (c).

Figure 12. The photocatalytic behavior (a) of praseodymium zirconate nanostructures (sample no. 8) on decomposition of various contaminants (cationic and anionic), (b) the photocatalytic behavior of the prepared praseodymium zirconate nanostructures (sample nos. 5 and 8), (c) the influence of the dosage of the nanostructured praseodymium zirconate (sample no. 8) on the methylene blue decomposition percentage and (d) the photocatalytic behavior of the nanostructured praseodymium zirconate (sample no. 8) under UV and visible light illumination.

Figure 13. Schematic diagram of the reaction mechanism of methylene blue photodegradation over the nanostructured praseodymium zirconate (a) and XRD pattern of the nanostructured praseodymium zirconate (sample no. 8) after photocatalytic performance.

Fig 1.

Fig 2.

Fig 3.

Fig 4.

Fig 5.

Fig 6.

Fig 7.

Benzene tricarboxylic

Citric acid

Succinic acid

Maleic acid

Salicylic acid

Propylenediamine

Ethylenediamine

Trimethylamine

Ammonia

Fig 8.

Fig 9.

Fig 10.

Fig 11.

Fig 12.

Fig 13.