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Electrophoretic deposition of hydrothermally synthesised Ag–TiO_2 hybrid nanoparticles onto 3-D Ni filters

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Ag–TiO_2 hybrid nano-powders were synthesised by hydrothermal method (HS) at 180 °C for 2 h. TEM and AFM analyses have shown that Ag nanoparticles embedded within the coarser TiO_2 particles have a spherical shape with a diameter of 7 nm whilst the size of the TiO_2 nanoparticles is found to be around 40 nm. It is also shown that the calcined (500 °C for 1 h) hybrid composite particles result in the formation of anatase TiO_2. The synthesised Ag–TiO_2 nanopowders were dispersed in ethanol to obtain stable colloidal suspensions and used to coat Ni-based filters using electrophoretic deposition (EPD) using an applied voltage of 30 V for 2 min. Overall, it is shown that hydrothermal processing is an effective way of synthesising nano-sized Ag–TiO_2 hybrid powders in a short time and EPD is a good way to get full coating onto 3-D Ni-based filters if stable suspensions are used.

1. Introduction

The application of nanoscale materials is an emerging area of nanotechnology [1] as they can be used in the applications, such as filtration where contaminant removals are taken place in liquid and gas environments. For instance, membranes that are impregnated with silver nanoparticles are presently being used for the water purification purposes [2] and the TiO_2 is being used in air purifiers to kill bacteria, fungi and algae [2]. TiO_2 in anatase or rutile crystalline forms is considered to be an efficient photocatalyst and has been widely used for photodegradation of various pollutants if they are synthesised in the desired shape and size [3,4]. The hydrothermal synthesis is a suitable technique for the production of Ag–TiO_2 nanoparticles since it facilitates the fabrication of even the complex materials with desired physical and chemical properties [5]. In the last two decades, there have been some studies on the synthesis and characterisation of Ag–TiO2 nanoparticles and coatings for different applications including anti-microbial materials [6–10].

Although many techniques, such as plasma spraying and sol gel coating are used to coat materials with different coating layers, electrophoretic deposition has gained significant attention in the last two decades as it is an effective way of coating materials for various applications in a short time and cost effective way [11,12].

Therefore, in the present work, the Ag–TiO_2 hybrid nanocomposite particles were synthesised by hydrothermal synthesis (HS) in a short time and Ni-based filters were coated using stable colloidal suspensions containing the Ag–TiO_2 hybrid particles by EPD.

2. Experimental work

Titanium isopropoxide (TTIP), silver nitrate ($AgNO_3$), 2-propanol (C_3H_8O) and polyvinylpyrrolidone (PVP) were used as the precursors. To obtain TiO_2 suspension, 20 mL 2-propanol and 10 mL TTIP were mixed and added drop-wisely to 400 mL solution of deionized water and nitric acid during magnetic stirring. Nitric acid was used to fix the pH at 1,5 before TTIP and 2-proponal addition. After the reaction was allowed to proceed for 24 h during stirring, the resulting solution was transparent. As a last step to produce Ag–TiO_2 nanopowder, the prepared solution obtained from $AgNO_3$ and PVP in 20 mL, deionized water (5 wt.% Ag and 3 wt.% PVP) was added drop-wisely to TiO_2 suspension and stirred for 30 min. The solution was put into the autoclave for the hydrothermal synthesis at 180 °C for 2 h. The synthesised Ag–TiO_2 nanopowder was calcined at 500 °C for 1 h. The colloidal suspension with solid-loading of 1 wt.% was prepared in ethanol by adjusting the pH to be 4 using HNO_3. The EPD coating cell with an electrode seperation distance of 20 mm was used and connected to a d.c. power supply. The Ni filter (the thickness of the filter is 2 mm) with the dimensions of 10 mm × 10 mm was put between two stainless steel electrodes (40 mm × 40 mm). Subsequently, nickel filter was coated using EPD (30 V for 2 min.). TEM, AFM and FEG SEM investigations were conducted to observe the size/shape of the particles and coating layers.

3. Results and discussions

Back-scattered (BS) and secondary image SEM micrographs indicate the general structure and the distribution of Ag within the hydrothermally synthesised Ag–TiO_2 nanoparticles, as shown in Fig. 1.

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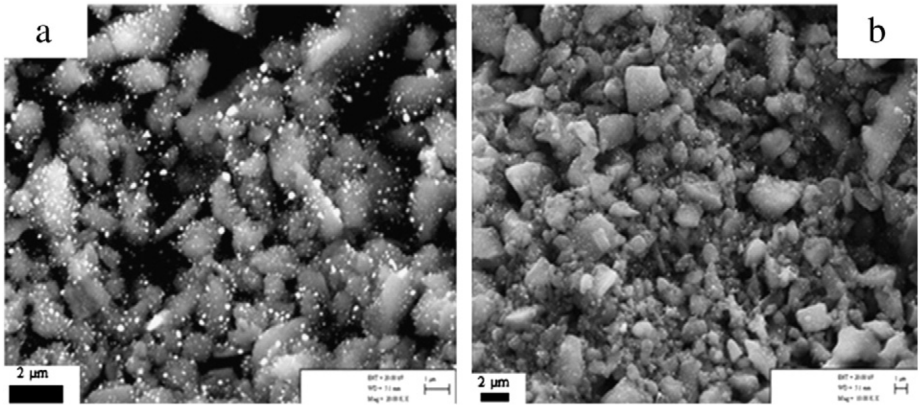

Fig. 1. Back-scattered image (a) and secondary electron image (b) of the Ag–TiO_2 hybrid nanopowders indicating the nano-scale structure of Ag particles (white particles in (a)) which is homogeneously distributed within the TiO_2 structure during HS.

Since the silver has greater atomic number than titanium and oxygen, silver nanoparticles seem brighter than titanium dioxide, as shown in BS image in Fig. 1a. It should also be noted from Fig. 1 that Ag nanoparticles are distributed homogeneously within the TiO_2 structure during HS leading to the formation of Ag–TiO2 hybrid nanocomposite powders.

It is confirmed by the TEM observations that the size of Ag particles is around 7 nm and the crystallites have a spherical shape as shown in Fig. 2 whilst the particle size of TiO_2 is about 40 nm. It is also observed in Fig. 2 that there is an interaction between the Ag nanoparticles and TiO_2 where most of the Ag nano-particles are actually embedded within TiO_2 and a few of them surrounds the TiO_2. A TEM EDS graph indicates the presence of Ag, Ti and O with a Ti/Ag ratio of 96/4 as a wt.%.

Fig. 3 shows the topographical (a) and 3-D (b) AFM images of Ag–TiO_2 hybrid nanocomposite particles where the dark part of the composite characterises TiO_2 nanoparticle in which smaller Ag particles are embedded. Fig. 3 also confirms the spherical nature of Ag–TiO_2 nanoparticles which is in a good agreement with the findings shown in Figs. 1 and 2.

Fig. 4 shows the SEM images of the Ni filter coated by EPD under 30 V of applied voltage for 2 min. The coating was successfully obtained under the conditions used and the inner and outer parts of the filters are homogeneously covered by Ag–TiO_2 particles, as shown in Fig. 4a. If kinetically stable suspensions are not used, only partial coverage of the Ag–TiO_2 particles can be obtained, as shown in Fig. 4b. It should also be noted from Fig. 4b that the inner part of the Ni filter is not fully covered due to the unstability of the suspensions. Coated images with

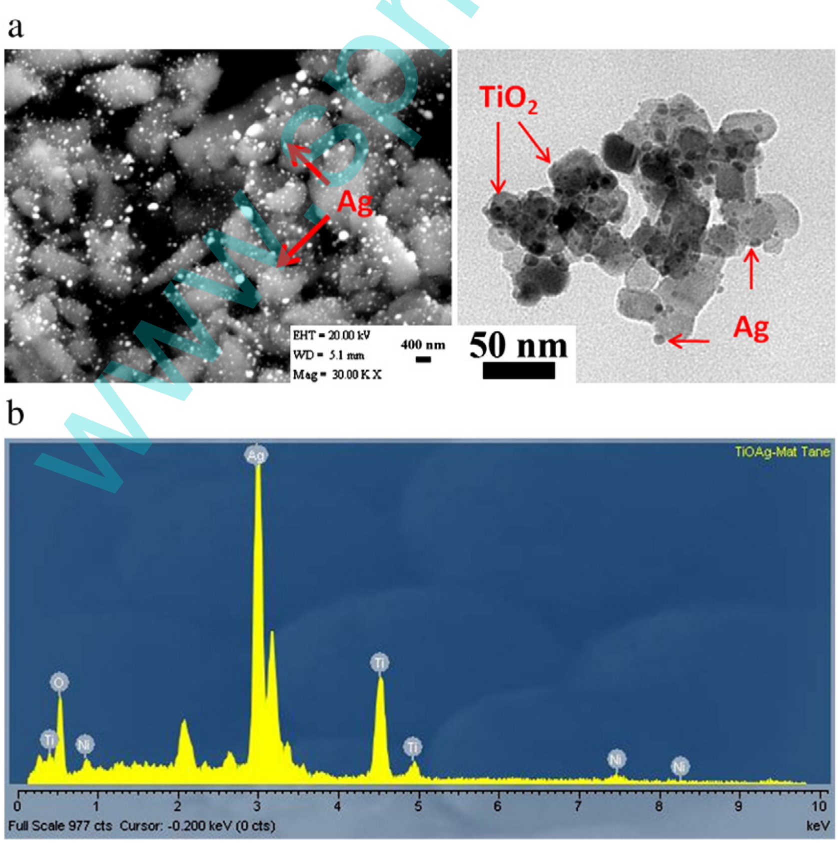

Fig. 2. The TEM image of the synthesised Ag–TiO_2 hybrid nanopowders (a) indicating the ultrafine Ag particles (7 nm) embedded within the TiO_2 particles and TEM EDS graph indicating a Ti/Ag ratio to be 96/4 as a wt.% (b).

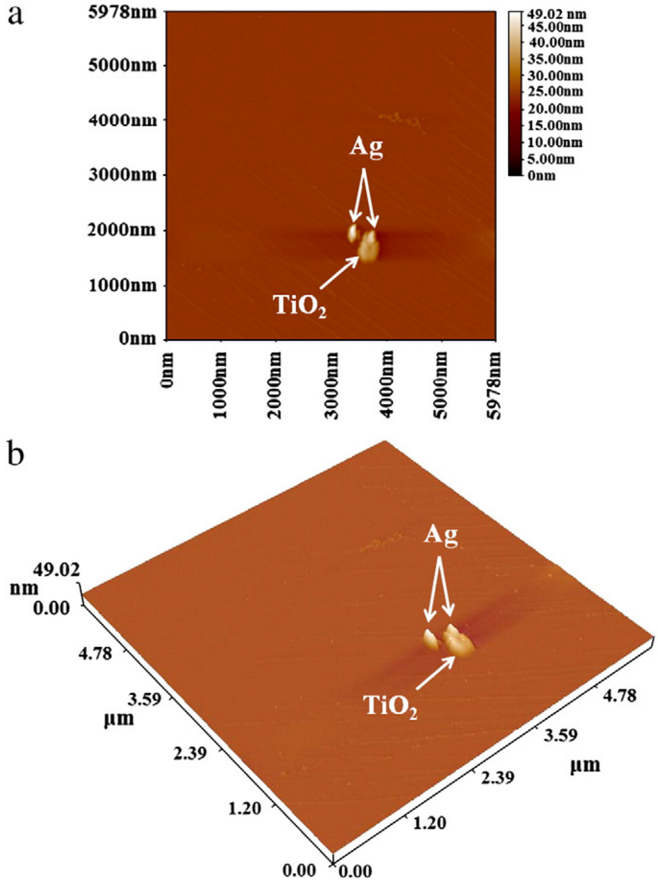

Fig. 3. The topographical (a) and 3D AFM (b) images of the Ag–TiO_2 composite particles synthesised.

higher magnification indicating the rough coating layer around the Ni filter are shown in Fig. 4c and d.

Fig. 5 shows the XRD analysis of the Ag–TiO_2 nanopowder after calcination at 500 °C for 1 h. Most of the peaks correspond to the presence of anatase TiO_2 and silver (Ag), as expected. As shown in Fig. 5, the most intense peak at 101, which occurs at $2\theta = 25.34°$, represents typical tetragonal anatase TiO_2. But, there is also a small amount of the peaks that can be attributed to the rutile phase, as marked in Fig. 5.

The production of Ag–TiO_2 hybrid nanoparticle synthesis via the assistance of the hydrothermal method is a new approach where reduction and adhesion of silver nanoparticles on TiO_2 surfaces are completed under hydrothermal conditions. During the production of Ag nanoparticles, PVP acts as a reducing agent and a particle stabilising agent. PVP may surround silver nanoparticles and prevent them from growing. This idea is clearly supported by Figs. 1–3 where Ag particles remain very small during HS.

Overall, it is shown in the present paper that hydrothermal processing is an effective way of synthesising nano-sized Ag–TiO_2 hybrid powders in a short time and EPD is a good way to get coating using those nano powders. HS provides very pure and nano-sized Ag–TiO_2 powders where spherical Ag particles with an average particle size of 7 nm are embedded within rectangular shape TiO_2 particles with an average particle size of 40 nm. Now, studies are underway to understand the relationships between HS parameters in terms of temperature and time and particle size and shape. The EPD parameters in terms of time and voltage will also be optimised for full deposition of 3-D Ni filters.

4. Conclusion

Ag–TiO_2 nano-composite powders are synthesised by hydrothermal method at 180 °C for 2 h. It is shown that spherical Ag particles with an average particle size of 7 nm are attached to TiO_2 particles

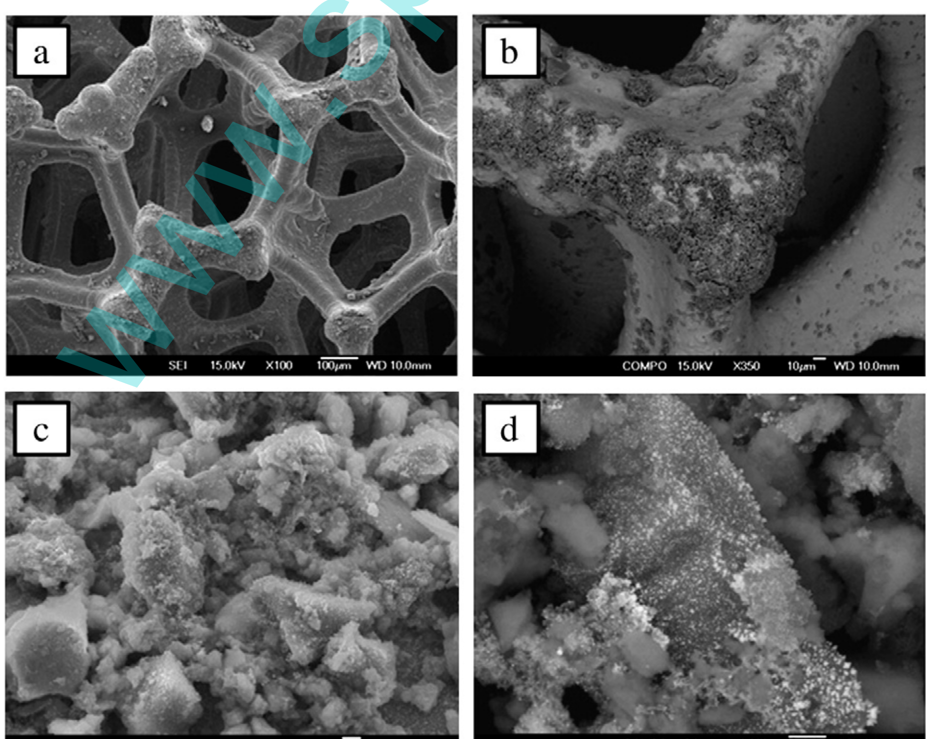

Fig. 4. Secondary electron images of fully deposited (a, c, d) and partially covered (b) the Ni filter after the EPD process.

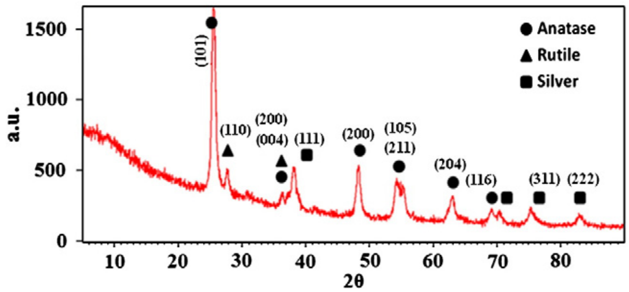

Fig. 5. XRD analysis of the Ag–TiO_2 nanopowder after calcinations at 500 °C for 1 h.

with an average particle size of 40 nm. The TEM observations also reveal that both TiO_2 and Ag nanoparticles have narrow size distribution. The accomplishment of the adhesion of the silver particles on to TiO_2 surfaces is considered beneficial for antimicrobial applications and now experiments are underway to determine the anti-microbial activity of the powders synthesised. XRD analysis reveals that the synthesis of TiO_2–Ag is accomplished in which the TiO_2 in the structure is mostly in the anatase phase after calcination at 500 °C for 1 h. It is also shown that EPD is an effective technique to coat 3-D shape filters in a short time. Using synthesised Ag–TiO_2 nanopowder stable colloidal suspension is obtained and it is used for the EPD process to coat the nickel filters.

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