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Silver doped titanium dioxide nanoparticles as antimicrobial additives to dental polymers

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ABSTRACT

Objective. The objectives of this in vitro study were to produce a filled resin containing Ag–TiO_2 filler particles and to test its antibacterial properties.
Methods. Ag–TiO_2 particles were manufactured using the ball milling method and incorporated into an epoxy resin using a high speed centrifugal mixer. Using UV/vis spectrophotometry investigations were performed to assess how the photocatalytic properties of the Ag–TiO_2 particles are affected when encased in resin. Adopting the bacteria colony counting technique, the antibacterial properties of Ag–TiO_2 particles and Ag–TiO_2 containing resins were assessed using *Streptococcus mutans* under varying lighting conditions.
Results. Ag doping of TiO_2 results in a band gap shift towards the visible spectrum enabling Ag–TiO_2 to exhibit photocatalytic properties when exposed to visible light. Small quantities of Ag–TiO_2 were able to produce a bactericidal effect when in contact with *S. mutans* under visible light conditions. When incorporated into the bulk of an epoxy resin, the photocatalytic properties of the Ag–TiO_2 particles were significantly reduced. However, a potent bactericidal effect was still achieved against *S. mutans*.
Significance. Ag–TiO_2 filled resin shows promising antimicrobial properties, which could potentially be used clinically.

1. Introduction

A truly antibacterial resin could find a number of clinical dental applications in both restorative dentistry and orthodontics. In restorative dentistry it could be used as a filling or denture base material, whilst in orthodontics it could be used as a bracket or bracket bonding material. Demineralisation of enamel is still one of the main complications of orthodontic treatment, particularly with fixed appliances [1]. The first sign of demineralisation may be the development of white spot lesions (WSL) on the enamel surface around the bracket margins, which if left unchecked can progress to cavitation. This

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whole process occurs more rapidly in orthodontic patients when compared to non-orthodontic patients [2,3]. Preventing enamel demineralisation and the formation of WSL is an important consideration for clinicians, as the lesions are unaesthetic and potentially irreversible. One cross sectional study showed that up to 50% of individuals undergoing fixed appliance therapy had non-developmental WSL compared with just 25% of controls [4]. Although the progression from WSL to cavitation is low (cavitation occurs in only 2% of WSL), the high incidence of WSLs is a significant factor where orthodontic treatment is being performed to improve aesthetics [5].

A Cochrane review assessing the effectiveness of methods used in the prevention of WSL formation concluded there was only evidence to support the use of daily 0.05% sodium fluoride mouthrinses in order to reduce their prevalence and severity [6]. Unfortunately it is often the case that patients at the highest risk of developing WSL are those least likely to comply with oral hygiene and mouth rinsing regimes. Therefore less patient dependent modes of delivery are required. Although the same Cochrane review concluded that the use of glass-ionomer cement for bracket bonding reduces the prevalence and severity of WSL, both glass-ionomer and resin modified glass-ionomer cements (RMGIC) have not gained widespread acceptance as orthodontic bonding agents, due to the reportedly lower shear bond strength and a lack of familiarity when compared to resin bonding systems and the associated acid etch technique [7].

A number of new technologies, principally fillers and coatings, have recently become available with potential antimicrobial properties. Although such coatings have the potential to be effective, they are also likely to be abraded and lost over time, or may corrode within the oral environment. For example if orthodontic brackets were to be coated with an antibacterial material it is unlikely it would be maintained on the bracket surface for the duration of a course of treatment [8].

Titanium dioxide (TiO_2), particularly in its nanoparticle form, has generated a great deal of interest over recent years, as it has numerous potential applications. A number of studies have demonstrated it to be an effective light activated photocatalyst, with strong bactericidal activity. However, its main disadvantage is its wide band-gap, meaning it is only really bactericidal when it absorbs UV light. With UV light being only a very small fraction of the solar spectrum (<5%), it means its activity is severely reduced under dark or visible light conditions, as would be found within the oral cavity [9]. In addition, traditional TiO_2 photocatalysis is effective only upon irradiation with UV-light at levels that could cause damage to human cells. As a result, researchers have conducted extensive studies on doping, sensitisation and covering the surface of the TiO_2 with dyes, in order to extend light absorption to the visible range. Doping TiO_2 with transition metal ions and/or anions is commonly used to this effect. This method creates intra-band gap states close to the conduction or valence band edges that induce visible-light absorption at the sub-band gap energies [9]. Ag+ modification of TiO_2 induces a decrease in the band gap energy, allowing visible light to activate the material's photocatalytic activity. This opens the possibility that such technology could be adopted within dental biomaterials and help prevent bacterial colonisation of intraoral appliances. Examples might include polymeric orthodontic brackets, bonding resins, dentures and intracoronal polymeric restorations. If the active particles were retained within the bulk of a polymer as well as at the surface, then any wear would simply expose more particles and thereby continue to confer an antimicrobial effect.

Table 1 – Four different volumes of $AgNO_3$ and Na_2CO_3 used for the construction of Ag–TiO_2 suspensions.

Sample	$AgNO_3$	Na_2CO_3
1 = 2% Ag	2.3 ml	2.5 ml
2 = 4% Ag	4.6 ml	5.0 ml
3 = 6% Ag	6.9 ml	7.5 ml
4 = 8% Ag	9.2 ml	10 ml

In this study the aims were to examine the effects of incorporating doped titanium dioxide nanoparticles into a polymer. The specific objectives were to investigate:

1. Free radical release at different silver doping concentrations of TiO_2 nanopowder.
2. The effect of varying the light conditions has on free radical release.
3. Free radical release when Ag–TiO_2 particles are incorporated into a bulk polymer.
4. The effect of silver doped TiO_2 on bacterial growth, both as a powder and when incorporated within a bulk resin.

2. Materials and methods

2.1. *Production of Ag–TiO_2 powders*

Silver doped photocatalytic TiO_2 powders were prepared by ball milling from commercial TiO_2 (P25) powders. Four different suspensions of Ag–TiO_2, were produced (Table 1). After drying, the powders were calcined at 400 °C for 90 min in a high temperature oven (Heratherm Oven, Thermo Scientific, UK) in order to decompose the silver salt and permit diffusion of the silver ions (Ag^+). Following calcination, the course powder produced was further ground using a centrifugal laboratory mixing and grinding machine (DAC150 Speedmixer, Hauschild Engineering, High Wycombe, UK).

To assess how the silver loading affected the band gap energy of the TiO_2, the powder samples were placed in a UV/vis Spectrophotometer (Lambda 35 UV/vis Spectrophotometer, Perkin Elmer, Massachussets, USA) and the readings plotted to show absorption at wavelengths ranging from 200 to 500 nm. Optical spectra were analysed using the Tauc model as reported by Impellizeri et al. [10]. Using this data the band gap shift for the TiO_2 and each of the four Ag–TiO_2 powders (2, 4, 6, and 8%) was determined.

2.2. *Testing Ag–TiO_2 powder for free radical release under different lighting conditions*

The Ag–TiO_2 powders were next tested for free radical release under visible light conditions. 0.05 g of samples 1–4 (Table 1) of Ag–TiO_2 powder and TiO_2 powder were added to beakers