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Pulsed laser deposition of Co_3O_4 nanoparticles assembled coating: Role of substrate temperature to tailor disordered to crystalline phase and related photocatalytic activity in degradation of methylene blue

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ABSTRACT

Cobalt oxide (Co_3O_4) nanoparticles (NPs) assembled coating have been prepared by reactive pulsed laser deposition of Co, in O_2 atmosphere, on Si or glass substrate ranging from room temperature to 250 °C. The NPs, having narrow size distribution with average values of around 25–50 nm, were characterized by Raman, X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy. The Co_3O_4 NPs synthesized at 150 °C comprise a mixed amorphous–nanocrystalline phase (that is unique property for catalysis) while complete crystallization of Co_3O_4 occurs at 250 °C with formation of spinel structure. Photocatalytic properties of Co_3O_4 NPs assembled coating for degradation of methylene blue solution under visible light irradiation are reported. The effect of H_2O_2 concentration and effect of pH variation on dye degradation rate has been reported. The reusability of the Co_3O_4 NPs assembled thin coating catalyst was further evaluated in several recycling runs. The activity of heterogeneous Co_3O_4 NPs assembled thin coating catalyst was compared with homogenous catalyst producing Co^{+2} ions in methylene blue solution.

1. Introduction

Textile dyes, releasing aromatic amines and potential carcinogens, are frequently found in trace quantities in industrial waste water. The increasing environmental concerns make it necessary to implement certain steps towards eliminating dyes from wastewater before discharging in the mainstreams. Advanced oxidation processes (AOP) involving active species like hydroxyl radical ($OH^{\bullet}$) with very high oxidation potential resulted to be most efficient route for dye degradation [1]. This radical generation occurs by processes such as direct photolysis of H_2O_2, photo-excitation of TiO_2, and Photo-Fenton reaction in presence of H_2O_2 and metal cations [2]. However, the first two methods require high intensity UV light while the Photo-Fenton reaction proceeds by absorption of visible light hence showing significantly higher efficiency.

Photo-Fenton reaction is very complex type of photocatalytic reaction which employs a mixture of H_2O_2 and ferrous ions (Fe^{2+} and Fe^{3+}) in acidic medium to generate the hydroxyl radicals in presence of light [3]. Due to the requirement of acidic medium with low pH (pH 3) the process results in large sludge residues. Other transition metal ions like Co^{2+} ions are found to be active even in neutral pH for generating hydroxyl radicals via Photo-Fenton process and this is a clear advantage over Fe^{2+} [4]. However, this kind of homogenous reaction produces additional impurity in the water by the dissolved metal ions (Fe^{2+} and Co^{2+}) thus avoiding its use on the commercial level. Hence the heterogeneous cobalt oxide catalyst has attracted great attention to generate hydroxyl radicals. The catalyst like Co_3O_4 has been considered for photodegradation of organic dyes in waste water treatment application because of its thermodynamic stability and desired catalyst properties [5–7]. Co_3O_4 nanorods prepared by complex pyrogenation method showed photocatalytic degradation of the three different dyes: reactive black, reactive turquoise, and reactive blue [8]. Small nanosized clusters of Co_3O_4 coated on PTFE (polytetrafluoroethylene) flexible coating are reported as novel and efficient supported photocatalysts in the fast discoloration of the azo-dye Orange II under simulated solar radiation in the presence of oxone [9].

Nano-structures of Co_3O_4 (nanoparticles, nanorods, nanowires, etc.) exhibit exceptional activity and selectivity in catalytic processes as compared to the corresponding bulk counterpart, especially because of their large surface-to-volume atomic ratio, size- and shape-dependent properties, and high concentration of under-coordinated active surface sites [10,11]. In the past, Co_3O_4 nanoparticles (NPs) have been synthesized primarily in powder

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