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Solvent effects on arc discharge fabrication of durable silver nanopowder and its application as a recyclable catalyst for elimination of toxic *p*-nitrophenol

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HIGHLIGHTS

- Long-lasting, low cost silver nanopowder (AgNP) is produced by arc discharge.
- The recyclable AgNP is used as a heterogeneous catalyst for purification of water.
- Highly toxic *p*-nitrophenol is efficiently converted to *p*-aminophenol by AgNP.
- Hydrogen is produced in the process as a clean source of energy from polluted water.

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ABSTRACT

Various types of nanosilver have been synthesized by a variety of methods, among them “arc discharge” stands with numerous advantages and calls for a much higher attention. Here, an unprecedented durable powder form of silver nanopowder (AgNP) is produced by DC arc discharge through a simple, convenient, and economical route, at a current of 5–10 A/cm^2. Effects of media are probed against the quality of the resulting nanoparticles. Among eleven media explored, glycerin/water (10% w/w) is found to afford the highest yield, purity, and relatively smaller size of AgNP with the desired morphology. To our joy, the as-prepared-AgNP proves efficient in catalytic green reduction of *p*-nitrophenol (PNP) which is one of the most potent water pollutants. Our reduction of PNP by $NaBH_4$ in the presence of AgNP in water is monitored by UV–Vis spectrophotometry. A provisional mechanism is proposed for this reaction which appears fast and completes in two minutes. The AgNP is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Hence, arc discharge fabrication of durable AgNP is maximized by adapting glycerin/water as the medium of choice; and the resulting AgNP catalyzes toxic PNP conversion into *p*-aminophenol.

1. Introduction

Nanotechnology is developing new materials and examining their properties by altering the particle size, morphology and distribution [1]. Nanoparticles have potential applications especially in fabrication of electronic devices, sensors, nonlinear optical materials, ultrafast data communication, optical data storage, photochemical catalysis, biomedicine, *etc.* [2–4]. Synthesis of metal nanoparticles has fascinated scientists because of their catalytic, optical, electronic, antimicrobial, and magnetic properties [5–9]. Transition metal nanoparticles are prepared and used extensively since they display unique physicochemical properties due to their size-induced quantum effects (large surface to volume ratio) and thus differ significantly from their bulk counterparts [10]. Between nanometals, Ag nanoparticles have attracted considerable attention as a result of its significant applications in fundamental sciences and nanotechnology [9]. Its characteristics strongly depend on the size, morphology, surrounding media, and aggregation state [11–16].

Normally, physical and chemical methods have been widely used for preparation of metal nanoparticles. The physical preparation includes sonochemical, photolytic, and radiolytic reductions, along with laser ablation, microwave, and ultrasound metal evaporation–condensation [17–20]. Pulsed wire evaporation (PWE) technique, a physical process, allows high production rate and particle size control with high efficiency, has been introduced to

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produce metal nanopowders, namely, Ni [21], Fe [22,23], Al [24,25], Cu [26,27], Ag [28–30] and so forth, or nano-powder alloys, such as brass [31], Pt–Ni [32], Cu–Ni [33], and Cu–Ni–P [34]. In this technique, a high power pulsed dc current passing through a thin metal wire leads to the wire explosion, and the large amount of heat energy causes the wire to melt, followed by subsequent evaporation and formation of plasma. The plasma formed during the process expands and cools when it interacts with a coolant such as an inert gas or liquid, and then nanoparticles are formed through the nucleation process [21,24,35,36].

The chemical methods incorporate reducing the metal ion precursors with alcohol, citrate, borohydride, polyol, N_2H_4, $Na_3(C_6H_5O_7)_5$, *etc.* [37–42].

In order to control the size of Ag nanoparticles and prevent its aggregation, it is often dispersed in a liquid or solid medium or embedded in a polymer matrix [10,16]. Actually, shrinking of Ag into nanosilver with large surface area makes it a highly effective catalyst for heterogeneous reactions [10,43]. Yet its performance depends on the selection of the catalyst support/matrices.

On the other hand, *p*-nitrophenol (PNP) is one of the most important intractable contaminants that can arise in industrial and agricultural wastewaters [10]. It is recorded in "*the U.S. Environmental Protection Agency List of Priority Pollutants*" [16,44,45]. To eliminate 1, the wastewater is often treated with a catalyst which reduces it into *p*-aminophenol (AmP) [10]. Most classic methods for reduction of such nitro compounds are costly, messy, and environmentally hazardous. They often use metallic reagents in the presence of an acid [6]. Therefore, safer and more economical synthetic routes are necessary. One method is employing $NaBH_4$ in water as the hydride source. But reduction of nitro groups with $NaBH_4$ in the absence of any catalyst is highly tedious. Many different metals including gold have been used to carry out this task [46–49]. Silver metal has not yet been employed, but its nanocomposites are used as heterogeneous catalysts for reduction of PNP [10,16,41,43,48,50]. These catalysts while are rather inexpensive and often reusable, carry the burden of lower catalytic activity than the homogeneous ones [10]. Hence, effort towards green preparation of heterogeneous, durable, economical nanocatalysts with enhanced activity is of great current interest.

Here we probe the effects of media on size, morphology, purity, durability, and yield of silver nanopowder (AgNP) fabricated by arc discharge; and examine its green application as a recyclable catalyst for easy and economical reduction of PNP.

2. Experimental section

2.1. Materials

Silver electrodes are prepared from 10 oz fine silver bullion from Switzerland. 4-Nitrophenol, $NaBH_4$ and solvents are obtained from Merck.

2.2. Preparation of AgNP

Silver electrodes, with 80° angle, are exposed to pulses of 5–10 A/cm^2 in different media. Products are separated as nanopowder, upon centrifuging and drying at 70 °C for 24 h.

Nanostructures are characterized using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuK = 0.9, radiation, $\lambda = 0.154056$ nm), at a scanning speed of 2°/min from 20° to 80° (2θ). In addition the particle shape and morphology are characterized by SEM (KYKY EM3200 – 25 kV) and TEM (Zeiss EM10C 80 kV). Size distribution is determined by Malvern Zetasizer ZEN3600. To prove the structural characterization of the samples, XRD is utilized. To estimate the average grain size and their quality with the (1 1 1) diffraction peak, Scherrer's equation is used [51].

2.3. Catalytic studies

Pure AgNP, prepared in glycerin/distilled water (10% w/w) at 5–10 A/cm^2, is employed as a heterogeneous catalyst for reduction of **1** by $NaBH_4$ in distilled water. This reaction does not progress without the catalyst under similar conditions. Specifically, 3 mL of **1** ($1.8 * 10^{-2}$ g/L) and 1 mL of freshly prepared $NaBH_4$ (4 g/L) in aqueous solution is placed in a quartz cuvette (optical path length 1 cm), and then 5 mg of the AgNP is added. Immediately after the addition, the UV–Vis absorption is recorded at an interval of 10 s (kinetics mode) to monitor the reaction (Fig. 1c).

3. Result and discussion

Size, morphology, and durability of nanosilver highly depend on its method of synthesis. Following our quest for stable nanomaterials [23,25,27,31], here we take up fabrication of durable AgNP, through arc discharge in different media. Consecutively, we report its application as a novel and recyclable catalyst for reduction of PNP, which is a potent water pollutant.

3.1. Fabrication of durable AgNP through arc discharge in different media

The current arc discharge fabrication, in different media, renders the product in powder form with different size and high durability. Specifically, our DC arc discharge technique involves explosion of silver rods by a current pulse between 5 to 10 A/cm^2. Fairly pure silver electrodes (99%) with diameters of 2 mm and lengths of 40 mm are used as anode and cathode. Arc experiment is initiated by slowly detaching the moveable anode from the static cathode. In order to maintain a stable discharge current between 5 to 10 A/cm^2, the cathode–anode gap is controlled at approximately 1 mm. Separating the electrodes increases the voltage, while bringing them close together decreases it. To sustain the arc inside the medium, the angle between the two electrodes is maximized to 80°. Gas bubbles are formed in the aqueous media during the arc process, due to the plasma vaporization/decomposition of the anode material and boiling plus decomposition of the medium. Generation of gaseous hydrogen and oxygen occurs through water decomposition (*i.e.* electrolysis). They appear as small bubbles which become partly dissolved. Hydrogen (molecular or atomic) escapes quickly from the water suspension and goes to the gas phase, since it neither adsorbs on the silver [30], nor significantly dissolves in water. However, oxygen (especially atomic) may adsorb and slightly react with the silver surface at room temperature. The escaping gas bubbles act as a condensing medium. The silver could easily create hydrogen bonds with water [9]. During arc discharge the temperature between electrodes can reach several 1000 °C, which cause etching in the medium [52]. The vaporized metal can be condensed more efficiently in the polar liquids than the gas phase [9]. These media pose rather low explosion risk. Again, they play a role in quenching and capping the atomized Ag vapor into dispersed solid nanostructures.

Our eleven experiments carry out explosions in seven aqueous media including: glucose/distilled water (10% w/w), glucose/distilled water (25% w/w), glycerin/distilled water (10% w/w), glycerin/distilled water (25% w/w), phenol/distilled water (5% w/w), $Mg(NO_3)_2 \cdot 6H_2O$/distilled water (0.01% w/w), and $Mg(NO_3)_2 \cdot 6H_2O$/distilled water (0.05% w/w); as well as four organic media including: xylene, ethylene glycol, ethyl acetate, and phenol/toluene (5% w/w) (Table 1).

Interestingly, chopped off slices of AgNP coatings are clearly shown in the SEM images (Fig. 2, Sample 2). Such coatings prolong the life time of the nanopowder, through preventing oxidation and