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# Reduction of Cr(VI) to Cr(III) using silicon nanowire arrays under visible light irradiation

Ouarda Fellahi[a,b], Alexandre Barras[a], Guo-Hui Pan[c], Yannick Coffinier[a], Toufik Hadjersi[b], Mustapha Maamache[d], Sabine Szunerits[a], Rabah Boukherroub[a,*]

[a] *Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), UMR CNRS 8520, Avenue Poincaré—BP 70478, 59652 Villeneuve d'Ascq Cedex, France*

[b] *Centre de Recherche en Technologie des Semi-conducteurs pour l'Energétique-CRTSE 02, Bd Frantz Fanon, BP. 140, Alger 7 Merveilles, Algeria*

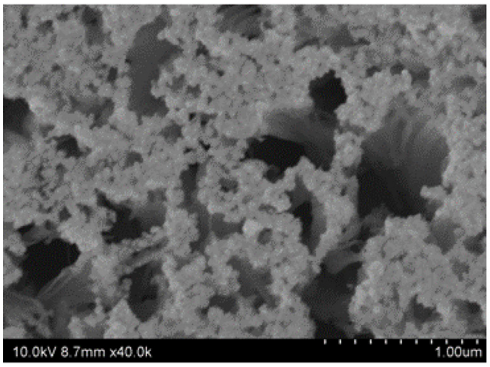
[c] *State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Dong Nanhu Road, Changchun 130033, China*

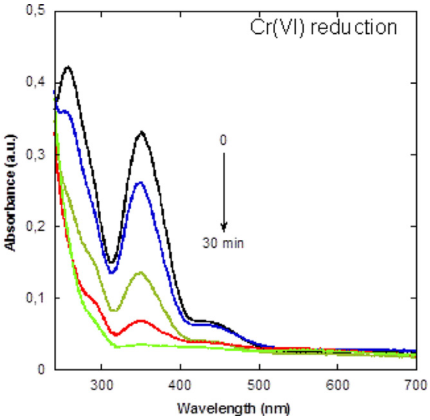
[d] *Laboratoire de Physique Quantique et Systèmes Dynamiques, Département de Physique, Université de Sétif, Sétif 19000, Algeria*

## HIGHLIGHTS

- Cr(VI) reduction to Cr(III) using silicon nanowires decorated with Cu nanoparticles.
- The reduction takes place at room temperature and neutral pH under visible light.
- The photocatalytic reduction was enhanced by addition of adipic or citric acid.

## GRAPHICAL ABSTRACT





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## ABSTRACT

We report an efficient visible light-induced reduction of hexavalent chromium Cr(VI) to trivalent Cr(III) by direct illumination of an aqueous solution of potassium dichromate ($K_2Cr_2O_7$) in the presence of hydrogenated silicon nanowires (H-SiNWs) or silicon nanowires decorated with copper nanoparticles (Cu NPs-SiNWs) as photocatalyst. The SiNW arrays investigated in this study were prepared by chemical etching of crystalline silicon in HF/$AgNO_3$ aqueous solution. The Cu NPs were deposited on SiNW arrays *via* electroless deposition technique. Visible light irradiation of an aqueous solution of $K_2Cr_2O_7$ ($10^{-4}$ M) in presence of H-SiNWs showed that these substrates were not efficient for Cr(VI) reduction. The reduction efficiency achieved was less than 10% after 120 min irradiation at $\lambda > 420$ nm. Addition of organic acids such as citric or adipic acid in the solution accelerated Cr(VI) reduction in a concentration-dependent manner. Interestingly, Cu NPs-SiNWs was found to be a very efficient interface for the reduction of Cr(VI) to Cr(III) in absence of organic acids. Almost a full reduction of Cr(VI) was achieved by direct visible light irradiation for 140 min using this photocatalyst.

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* Corresponding author. Fax: +33 3 62 53 17 01.
*E-mail address:* rabah.boukherroub@iemn.univ-lille1.fr (R. Boukherroub).

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## 1. Introduction

Hexavalent chromium Cr(VI) is a priority pollutant in many countries and Cr(VI) contamination of soil and groundwater is a significant problem worldwide [1]. The extensive distribution of this pollutant in the environment is due primarily to its application in a wide range of industries such as the production of stainless steel, in plating, refractory industry and tanning of leather, pigment and chemical industry, wood treatment, *etc.* Cr(VI) is toxic to humans, animals, plants and microorganisms. In contrast, Cr(III) is much less toxic and an essential nutrient for human and animals; Cr(VI) reduction to Cr(III) is thus very important in the remediation of environmental sites contaminated by chromium. Several research reports have focused on the reduction of Cr(VI) to Cr(III) using semiconductor catalysts such as $TiO_2$ [2–4], $WO_3$-doped $TiO_2$ nanotubes [4], $NaTaO_3$ [5], NiO/$TiO_2$ [5], ZnO/$TiO_2$ composite [6], NiO [7], bismuth oxychloride [8] or ZnO nanoparticles [9] under UV or laser irradiation. The photocatalytic reduction of Cr(VI) can also be achieved under visible light irradiation when nanocomposites of $TiO_2$ and $SnS_2$ [10], bismuth-doped ordered mesoporous $TiO_2$ [11], $TiO_2$/graphene [12], $SnS_2/SnO_2$ [13] nanocomposite, N-doped $TiO_2$ [14], and g-$C_3N_4$ [15] are used as photocatalysts.

When a semiconductor suspension was irradiated with UV light ($\lambda < 387$ nm), the photo-induced electrons are responsible for the photocatalytic reduction of Cr(VI). The UV or visible photocatalytic reduction of Cr(VI) to Cr(III) generally proceeds very slowly, because the accompanying oxidation of water to oxygen is a kinetically slow process [16]. Addition of organic donors accelerates significantly the UV photocatalytic reduction of Cr(VI), due to enhanced charge separation of photo-induced hole/electron pairs by the simultaneous reduction/oxidation reactions [17–21].

Although bulk silicon displays a small band gap (~1.1 eV), it has so far not been investigated in heterogeneous photocatalysis because its valence band is not positive enough to oxidize organic pollutants. In the last years, it has been established that silicon in its nanostructured form is, however, an effective photocatalyst for oxidation of organic dyes and selective oxidation of aromatic molecules [22–29], as well as for the reduction of graphene oxide (GO) [30]. The photocatalytic efficiency of hydrogenated SiNWs for the degradation of rhodamine B (RhB) and oxidation of benzyl alcohol to benzoic acid was highlighted for the first time by Shao et al. [23]. The higher performance of H-SiNWs compared to SiNWs decorated with Pd, Au, Rh or Ag NPs for the degradation of RhB was also demonstrated [23]. We have recently shown that decorating SiNWs with Cu NPs enhances the photocatalytic performance of the substrate for the photodegradation of RhB under visible light irradiation [24].

While the photocatalytic activity of SiNWs substrates for the oxidation of dyes and organic molecules has been described, there has been no report on the use of these substrates for the reduction of hexavalent chromium Cr(VI) under visible light irradiation. The goal of our work is to investigate the efficiency of SiNWs catalysts for the photoreduction of Cr(VI) to Cr(III) under visible light irradiation with and without organic additives. The photocatalysts consist of H-SiNWs and SiNWs decorated with Cu NPs. In the absence of organic additives, it was found that H-SiNWs was not efficient for the Cr(VI) reduction under visible light irradiation, while Cu NPs-SiNWs led to almost full reduction of Cr(VI) after 140 min irradiation. Addition of citric acid (5 mM) into the solution accelerated significantly the reduction rate.

## 2. Results and discussion

The SiNW arrays investigated in this study are obtained by metal-assisted chemical etching of p-type silicon wafers (boron-doped, 0.009–0.01 Ω-cm resistivity) in HF (5 M)/$AgNO_3$ (0.035 M) aqueous solution at 55 °C for 30 min [30–32]. The technique is easy to carry out and the formation of the silicon nanostructures takes place at relatively low temperature. As shown in scanning electron microscopy (SEM) images in Fig. 1, this one step chemical etching process produces vertically oriented SiNWs with a length of ~5.6 μm and a diameter size in the range of 20–100 nm (Fig. 1A and B). EDX analysis of H-SiNWs substrate shows a strong signal from Si element and a small contribution from oxygen (Fig. 1C). The presence of oxygen in the EDX spectrum is most likely due to partial oxidation of silicon upon exposure to ambient.

Cu-decorated SiNW arrays are prepared by the electroless deposition technique [24,30,33]. In aqueous solutions, metal ions with redox potential greater than hydrogen attract electrons from Si atoms and are reduced to the atomic form. In diluted HF-solutions, Cu adheres on the Si surface easily and deposits locally in a particle form [34]. This technique has been applied for deposition of Cu nanostructures on porous silicon [35,36]. Electroless deposition of Cu on SiNW arrays occurs according to the following cathodic reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

The deposited metal atoms first form nuclei and then nanoclusters to give nanoparticles. This reaction is accompanied by silicon oxidation:

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^-$$

The role of HF in this chemical process is to dissolve the $SiO_2$ layer. Fig. 1D and E displays SEM images of the resulting SiNWs substrates decorated with Cu nanoparticles. Because of the concentration gradient of metal ions, more nanoparticles tend to grow at the tips of the nanowires [37]. Thus, the metal nanoparticles aggregate and grow larger, while the SiNWs become tapered. From the top-view SEM image in Fig. 1D, one sees that the nanowires are stuck to each other to form bundles. This phenomenon is most likely due to van der Waals attraction between the nanowires upon drying. Alternatively, it was also suggested that some nanowires may be left undetached due to inhomogeneous etching induced by a random Ag particle distribution [38]. A high magnification SEM image suggests that the size of the surface-deposited Cu NPs is in the range of ~50–100 nm (Fig. 1E). In contrast to H-SiNWs, the EDX spectrum of the Cu NPs-SiNWs substrate exhibits signals due to Si and Cu, and a small contribution from oxygen (Fig. 1F). The results are in good agreement with copper deposition on the nanowires. The presence of oxygen in the EDX spectrum is most likely due to partial oxidation of silicon upon exposure to ambient.

For TEM imaging analysis, the as-etched SiNWs or Cu NPs-SiNWs were scratched from the silicon substrate carefully and then were dispersed in ethanol by ultrasonication. Fig. S1 displays the TEM images of SiNWs. One SiNW of up to ~2.5 μm in length and ~150 nm in diameter was imaged in Fig. S1A. However, a closer observation on a selective area of this long SiNW (inset of Fig. S1A) indicates that the nanowire is porous with pore diameter of ~10 nm. In addition, some much shorter SiNWs or agglomerated/porous particles always appear upon extensive TEM observation, most probably due to the breaking of as-etched SiNWs during post-treatment consisting of scratching and ultrasonication. The high resolution TEM image taken on the long SiNW clearly shows the lattice fringes of diamond-like silicon (Fig. S1B). The interplanar spacing of ~0.31 nm is in good agreement with the *d*-spacing of (1 1 1) crystalline plane. SAED analysis is also performed on the SiNW. In most cases, the patterns consist of many regularly arranged diffraction spots, which implies the single crystallinity of the SiNWs even though they are porous. Such a feature is actually